CHAPTER VII

DISCUSSION

In the preceding chapters, effective methods for the evaluation of the polaron energy expressions for various cases and situations have already been presented. An outline of the theoretical arguments and the subsequent conclusions, the results of numerical calculations, and some further recommendations for future investigations will be presented in this chapter.

VII.1 Conclusions

In the present research, the path integral theory has been applied to the Fröhlich idealized polaron model in order to evaluate the polaron energy. The polaron has been considered as a single slow conduction electron in an ionic crystal, that interacts with the polarization field arising from the lattice vibrations.

In an ionic crystal, there are at least two positive and negative charged ions per unit cell giving rise to three acoustic and three optical modes of lattice vibration. In the acoustic modes, the positive and negative ions within each cell vibrate essentially in phase with one longitudinal and two transverse modes for each wave vector $\underline{k}$. The frequencies of the acoustic vibrational modes are low. The associated lattice potential energy depends on the complicated interactions

between neighbouring unit cells, thus the frequencies of these modes depend on the wave vector $\underset{\sim}{k}$. In the optical modes, the two ions within each cell vibrate essentially out of phase with two transverse modes and one longitudinal mode for each wave vector $\underset{\sim}{k}$. The frequencies of the optical modes of lattice vibration are high and the principal contribution to the associated lattice potential energy arises from the interactions within a unit cell. Therefore, the frequencies of these modes are not very sensitive to the phase relations between unit cells, and consequently these vibrational modes are assumed to be characterized by a constant frequency independent of $\underset{\sim}{k}$.

The constant frequency approximation is suitable for the polaron arising from the slow electron but is not so satisfactory for short wavelengths where the phase differences from one unit cell to another are significant. Thus it is appropriate to treat the polaron as an electron dressed by the phonons of optical vibrational modes, which have a large probability to be carried along with the moving electron. Furthermore, the electron-phonon interaction is very strong for the longitudinal modes, the frequencies of which can justifiably be regraded as being constant. For the transverse modes, in which the ions vibrate in the direction normal to the direction of propagation, the divergence of the polarization field vanishes. Therefore the interaction between the electron and these vibrational modes can be neglected.

Accordingly, the polaron can be described as an electron moving in the cloud of phonons arising from the longitudinal optical modes. The strength of the interaction is measured by the dimensionless coupling constant $\propto$, which can be roughly classified into three regions. There are highly polar substances, such as the alkali halides, with $\propto > 3$; intermediate cases, such as the silver halides, with $\propto \sim 1.5$; and weakly polar crystals, such as the compound semiconductors, with $\propto < 1$.

The polaron under consideration is in the region of strong coupling since it is created in an ionic crystal with the strong coulomb interaction. This is in contrast to the polaron in covalent crystals, for which the interaction between the electron and lattice ions is very weak. The crystal has been assumed to be electrically isotropic, and indeed it has been treated as a macroscopic dielectric continuum instead of the ordered arrangement of positive and negative lattice ions. Actually this approximation is quite valid for the case of a large polaron that is of our particular interest.

Physically, the situations of the small and the large polarons are rather different. The small polaron is created in a narrow conduction band, with the conduction from a lattice site to its neighbouring site taking place by a hopping process. In contrast, the conduction of the large polaron is relatively smooth and occurs by means of a band

type process. The small polaron is in a rather localized state in the sense that the electron-lattice interaction is very strong, and the electron often circulates and spends a long time in the immediate vicinity of a lattice ion. As the temperature increases, its mobility is increased as a result of the thermally activated hopping from one localized state to another. On the other hand, the motion of the large polaron is mainly controlled by its occasional scattering caused by lattice vibrations. Because the lattice ions vibrate very vigorously at high temperatures, the mobility of the large polaron decreases with increasing temperature.

After some physical discussion of the polaron behaviours, the steps of our theoretical investigation were then proceeded as follows. The classical Lagrangian of the polaron was determined first. On computing this, the electrons intrinsic to the crystal, i.e., the electrons in all the filled bands, were assumed to follow instantaneously the ionic displacements of the lattice vibrations and the motion of the slow electron in the conduction band. This is certainly a reasonable assumption in view of the fact that the frequencies of the electrons in the filled bands are much higher than the lattice frequencies. The periodicity of the lattice ions was taken into account by representing the periodic potential in terms of an effective mass m^*.

It was found useful to convert the polaron classical Lagrangian to the form of the quantum mechanical Lagrangian. For the behaviour of the electron could then be discussed

separately by applying the path integration to average out the contributions from the phonons. Thus the interaction between the electron and the lattices with many vibrational degrees of freedom could be conveniently represented by the interaction of the electron with a fictitious particle through the nonlocal coulomb potential. The polaron properties were then described by the action and this formed an important basis for the subsequent studies of the various polaron problems using the path integral formalism.

The polaron action at absolute zero temperature was derived in Section III.1, and was given by

$$S = -\frac{1}{2}\int_0^\infty \left[\frac{d\underline{r}_{el}}{dt}\right]^2 dt + \frac{\alpha}{2^{3/2}}\iint_0^\infty dt\,ds\,\frac{e^{-|t-s|}}{\left|\underline{r}_{el}(t)-\underline{r}_{el}(s)\right|}. \quad (7.1)$$

For the case of finite temperatures, it was given by

$$S = -\frac{1}{2}\int_0^\beta \left[\frac{d\underline{r}_{el}}{dt}\right]^2 dt + \frac{\alpha}{2^{3/2}}\left[\frac{e^\beta}{e^\beta-1}\iint_0^\beta dt\,ds\,\frac{e^{-|t-s|}}{\left|\underline{r}_{el}(t)-\underline{r}_{el}(s)\right|} + \frac{1}{e^\beta-1}\iint_0^\beta dt\,ds\,\frac{e^{|t-s|}}{\left|\underline{r}_{el}(t)-\underline{r}_{el}(s)\right|}\right] \quad (7.2)$$

as determined in Section IV.1 .

After the phonons have been averaged out, their effect acting on the electron is taken into account by the trapping of the electron in the retarded coulomb potential depending on its own positions at two different times t and s. This is contributed in the second part of the action. The reaction of the phonons on the electron depends on the time difference |t-s| and the electron distance between these times. The

disturbance in the past time, arising from the fact that the lattice distortion produced by the moving electron takes some time to relax, still survives. At absolute zero temperature the phonons are in the ground state initially and also finally so that the electron is dressed by the cloud of virtual phonons. In the case of finite temperatures there are the real phonons in the initial and final states. The effect of the phonons on the electron, contributed in the second part of the action with the strength of the electron potential energy, depends on the average number of the phonons $\bar{n} = \frac{1}{e^{\beta\omega_L}-1}$ in each mode. It should be reminded that the units used are such that the electron effective mass and its accompanying longitudinal optical phonon frequency ω_L are unity. The time development of the electron is closely related to the temperature development. Initially the electron may be considered to be at infinitely high temperture, and then it reverts to an arbitrary temperature $T = \frac{1}{k\beta}$ on a slowly cooling process. To attain the polaron state at absolute zero temperature, it is required to take infinite time in the development. In the case of a polaron state at arbitrary finite temperatures the time interval is finite, as given by $(0,\beta)$. The action (7.2) which describes the polaron at finite temperatures is reduced to depict the polaron state at absolute zero temperature by taking $\beta \rightarrow \infty$. Consequently, the action (7.2) becomes (7.1) and the average number of phonons $\bar{n} = \frac{1}{e^{\beta\omega_L}-1}$ is zero at absolute zero temperature.

As the path integration of the polaron action could not be carried out directly, an appropriate trial action had to be introduced. When the variational principle had been applied, we obtained the variation of the ground state energy as

$$E_1 - \frac{\langle S-S_1 \rangle}{\mathcal{J}} \geqq E_g \qquad , \qquad (7.3)$$

at absolute zero temperature. For the polaron state at finite temperatures, the above expression was replaced by the variation of the free energy

$$F_{tr} = F_1 - \frac{\langle S-S_1 \rangle}{\beta} \geqq F \qquad . \qquad (7.4)$$

In or derto obtain the upper bound to the ground state energy and the trial free energy, the average values of the exact and trial actions, $\langle S \rangle$ and $\langle S_1 \rangle$, were required. This led to the attempt to find $\langle \exp[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s))] \rangle$, which turned out to be a very important step in the solution of several problems in this research.

In determining the average of $\exp[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s)]$, we used the path integration measured by the trial action S_1. By using the Gaussian integral method the path integral could be carried out, and we thus obtained

$$\langle \exp[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s))] \rangle = \exp[\frac{i\underset{\sim}{K}}{2} \cdot (\underset{\sim}{\bar{r}}_{el}(t) - \underset{\sim}{\bar{r}}_{el}(s))] , (7.5)$$

which implied the knowledge of the classical path $\underset{\sim}{\bar{r}}_{el}(t)$.

At absolute zero temperature, the integro-differential equation for the classical paths could be easily converted into the ordinary fourth order differential equation. This equation was solved by using Laplace transformation and ignoring some transient terms.

For the case of finite temperatures, the integro-
differential equation was more complicated. The difficulty
in solving this equation could be avoided by representing the
path integral of the trial action S_1 by that of a simple
physical system with the Lagrangian introduced by Osaka. It
was given in Section V.2 by

$$L = \tfrac{1}{2}\dot{\underset{\sim}{r}}^2 + \tfrac{1}{2}M\dot{\underset{\sim}{R}}^2 - \tfrac{1}{2}k(\underset{\sim}{r}-\underset{\sim}{R})^2 + \underset{\sim}{f}(t).\underset{\sim}{r} \ . \tag{7.6}$$

The final result obtained from this treatment depends on the
variables R_1 and R_2 which can then be integrated out under
the condition $R_1 = R_2$. It differs from the former treatment
where the coordinates representing the fictitious particle
in the trial action have first been eliminated.

It is reasonable to expect that if the trial action S_1
is chosen as that of the many coupled paritcle model with
more adjustable parameters, we should obtain a more accurate
result. Thus the improvement of the polaron theory at absolute
zero temperature has been performed by introducing two addit-
ional parameters to the original Feynman trial action. In
this case, the integro-differential equation for the classical
paths has been converted into the sixth order differential
equation instead of the original fourth order differential
equation. We can then conclude that the trial action of the
n coupled particle model would give a $2n^{th}$ order differential
equation. Similarly, if the trial action has N parameters
we should obtain a $(N+2)^{th}$ order differential equation.

The improvement of the polaron theory at finite temperatures has been performed by using the trial action of the three coupled particle model with four parameters. There has been a difficulty in determining $\left\langle \exp\left[i\underset{\sim}{K}\cdot(\underset{\sim}{r}_{el}(t)-\underset{\sim}{r}_{el}(s))\right]\right\rangle$ since the integro-differential equation for this case is rather complicated. However, we have a very useful guidance from the results and conclusions of the previous treatments. The more general treatment has been attempted by introducing the model Lagrangian

$$L = \tfrac{1}{2}\underset{\sim}{\dot r}^2 + \tfrac{1}{2}M_1\underset{\sim}{R}_1^2 - \tfrac{1}{2}k_1(\underset{\sim}{r}-\underset{\sim}{R}_1)^2 + \tfrac{1}{2}M_2\underset{\sim}{R}_2^2 - \tfrac{1}{2}k_2(\underset{\sim}{r}-\underset{\sim}{R}_2)^2 + \underset{\sim}{f}(t)\cdot\underset{\sim}{r}. \quad (7.7)$$

The physical meaning of L is that of two particles joined to one particle with unit mass by two springs with force constants k_1 and k_2. This classical Lagrangian depicts the physical system that is the same as the polaron system described by the consequent trial action, under the conditions $\omega_1 = \omega'_1$, $M_1\omega_1'^3 = 4C_1$, and $\omega_2 = \omega'_2$, $M_2\omega_2'^3 = 4C_2$. The relationship between the two systems is as follows. The particle with coordinates $\underset{\sim}{r}$ is just the electron. The two particles with coordinates $\underset{\sim}{R}_1$ and $\underset{\sim}{R}_2$, respectively, are represented by the two fictitious particles in the trial action the coordinates of which are first to be eliminated.

It is appropriate to separate the model Lagrangian into sets of independent harmonic oscillators in the center of mass coordinates. The classical Lagrangian (7.6) can be successfully separated into two forced harmonic oscillators with

coordinates q and Q, as mentioned in Section V.3. Unfortunately, the model Lagrangian (7.7) cannot be identified with the Lagrangian for the set of three independent forced harmonic oscillators with the center of mass coordinates q_1, q_2 and Q_0. So the consequent complications do appear in the improved polaron theory at finite temperatures as presented in Chapter VI.

VII.2 Comparison of Results

The results of numerical calculations of the energy expression (3.70) performed by Schultz[7] are presented in Table 1. The parameters, the polaron ground state energies for various electron-phonon coupling constants $\propto$, and the resulting self energies obtained from other theories[8,9,22] are included in this tabulation. On comparing these results, the Feynman polaron ground state energies obtained by using the path integral technique are seen to be better than those of other theories for the whole range of coupling constants $3 < \propto < 11$. This should clearly indicate a great advantage in using the path integral formalism.

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22 T.D. Lee, F.E. Low, and D. Pines, Physical Review, 90 (1953) 297.

Table 1 Feynman's parameters and comparison of ground state energies

α	3	5	7	9	11
$v/\hbar\omega_L$	3.44	4.02	5.81	9.85	15.5
$\omega/\hbar\omega_L$	2.555	2.13	1.60	1.28	1.15
$E_g/\hbar\omega_L$					
Feynman	-3.1333	-5.441	-8.1127	-11.486	-15.710
Lee, Low, and Pines	-3.0000	-5.0000	-7.0000	- 9.000	-
Lee and Pines	-3.10	-5.30	-7.58	-9.95	-12.41
Gross	-3.09	-5.24	-7.43	-9.65	-11.88
Pekar, Bogolubov and Tyablikov	-	-	-6.83	-10.31	-14.7

Table 2 Improved Feynman's parameters and comparison of ground state energies

| α	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0
v_+	12.63311	12.73754	12.69110	12.80481	12.91203	13.02719	13.05363	13.08958
ω_1	12.48989	12.52077	12.39799	12.43427	12.45977	12.48812	12.41545	12.16584
v_-	2.12389	2.20729	2.28588	2.37936	2.47885	2.5878	2.69957	2.90375
ω_2	1.96874	1.96006	1.93677	1.91388	1.88115	1.83845	1.77847	1.57952
$E_g/\hbar\omega_L$								
Improved Feynman	-1.01328	-1.53076	-2.0564	-2.59106	-3.1358	-3.69190	-4.2610	-5.4472
Feynman	-1.0130	-1.5302	-2.0554	-2.5894	-3.1333	-3.6885	-4.2565	-5.4401
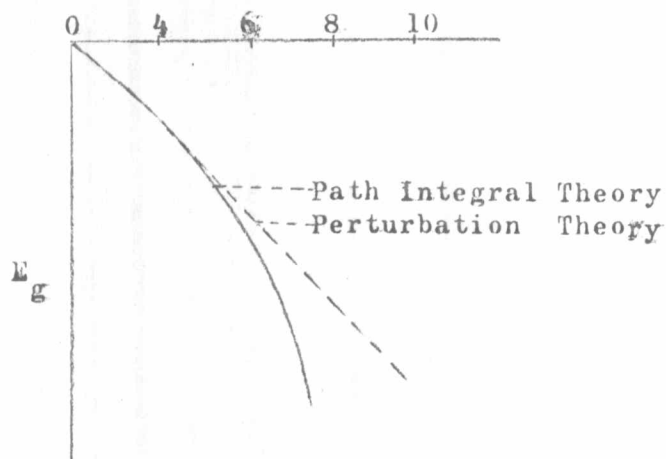
Fig. 7 Polaron ground state energy.

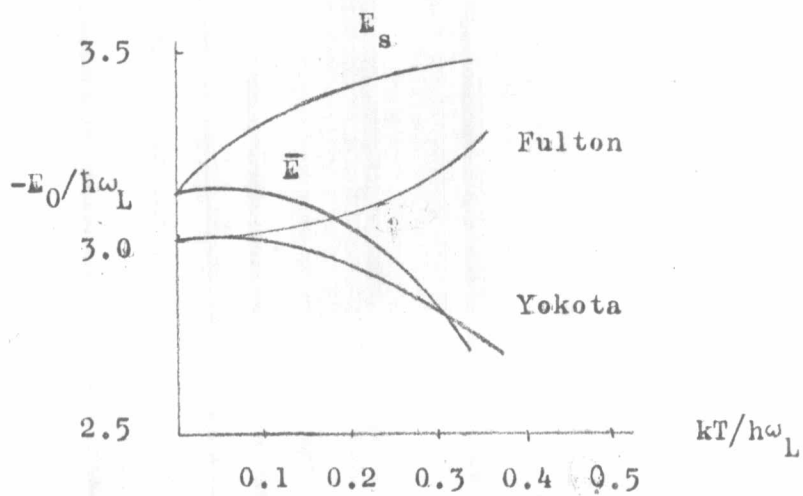

Fig. 8 Polaron self energy and average energy for $\alpha = 3$.

The Feynman polaron ground state energies versus the coupling constants α are plotted in Fig.7 and compared with the result obtained from the second order perturbation theory. As can be seen in this figure, the ground state energies become lower as the coupling constants increase. In the weak coupling region, the results obtained from both theories are in good agreement. However, in the strong coupling region, the ground state energy given by the path integration is definitely lower than that of the perturbation theory. This reflects the fact that the perturbation theory is only applicable to the polaron with a very weak coupling constant.

After the Feynman theory has been improved, the new energy expression is given by (4.49). The numerical calculations have been performed by Okamoto and Abe[14]. The four variational parameters v_+, v_-, ω_1 and ω_2 which give the minimum values of the ground state energies, and the ground state energies for several coupling constants in the region $1 \leq \alpha \leq 5$ are presented in Table 2. A comparison of the ground state energies before and after the improvement is also presented in the tabulation.

The improvement gives better ground state energies than those of Feynman in the region $1 \leq \alpha \leq 5$ but the corrections are not large. Presumably, it may be due in part to some inappropriateness in representing the exact coulomb potential by two harmonic potentials, especially in the nonlocalized state.

The polaron self energy and average energy expressions (5.56) and (5.55) have been minimized with respect to the

parameters ω and v for the coupling constant $\alpha = 3$ by Osaka[15]. The results obtained in the region of low temperatures, $0 < \frac{kT}{\hbar\omega} < 0.6$, are shown in Fig.8. A comparison with the results of Fulton[23] and Yokota[24] is also presented. As can be seen in this figure, the average energy obtained by this treatment agrees qualitatively with the results obtained by Yokota. But a qualitative difference is obtained in the comparison with that of Fulton, which may be due to the neglect of the entropy part in the free energy of a polaron.

A qualitative explanation of the temperature dependence of the polaron energy is as follows. As the temperature rises, there is more gain in entropy when phonons are increasingly free from the electron that has been dressed by the cloud of phonons. Therefore the average energy is decreased, whereas the self energy is increased. When the temperature falls, the self energy is decreased, tending towards the ground state energy at absolute zero temperature.

VII.3 Recommendations

Several polaron theories already discussed in Chapters III, IV, V and VI can be successfully related to each other by considering further the expression $\left\langle \exp\left[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s)) \right] \right\rangle$

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[23] T. Fulton,"Self-Energy of the Polaron for Intermediate Temperature.", Physical Review, 103 (1956) 1712.

[24] T. Yokota, "Interaction in the Electron-Lattice System(I) Correspondence Principle.", Busseiron-Kenkyu, 69 (1953) 137.

that evidently has been of much importance in the evaluation of the polaron energy.

As the polaron systems can be characterized by the parameters C_1, C_2, ω_1, ω_2, and β, the various limiting cases of the variational parameters C and the temperature parameter β will be considered.

1) For $C_2 = 0$ or $v_+^2 = v_1^2$, $v_-^2 = v_2^2 = \omega_2^2$, the result of the improved polaron theory of Abe and Okamoto reduces to that of the original Feynman polaron theory under the conditions $v_1 = v$ and $\omega_1 = \omega$.

2) For $\beta = \infty$, the Osaka polaron theory at finite temperatures reduces to the original Feynman theory.

3) If we fix β, as $C_2 \rightarrow 0$, the improved polaron theory at finite temperatures will be reduced exactly to the Osaka theory, and will become the original Feynman theory as β approaches infinity.

4) For fixed C_2, as $\beta \rightarrow \infty$, the improved polaron theory at finite temperatures reduces to the improved polaron theory of Abe and Okamoto at absolute zero temperature.

We note that one of the expressions for $\left\langle \exp\left[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s))\right]\right\rangle$ presented in Chapter VI successfully reduces to those of all the previous theories but it has been obtained only under special conditions. For the general treatment, we have obtained a new expression, within which the second term is in a rather incomplete form so that numerical calculations and further investigations are still needed for its full justification.

Other interesting problems which should be considered in the immediate future include an improvement of the trial action of Abe and Okamoto by using six parameters, from which we expect to obtain one more factor of the form $(1-e^{-v_3|t-s|})$ in the expression for $\langle \exp[i\underset{\sim}{K} \cdot (\underset{\sim}{r}_{el}(t) - \underset{\sim}{r}_{el}(s))] \rangle$, numerical calculations of the polaron energies at various coupling constants, and a further improvement of the polaron effective mass at finite temperatures. The evaluation of the polaron energy by including the higher order terms of the expansion $\langle \exp(S-S_1) \rangle$ in terms of the cumulants, viz.,

$$\exp\left\{ \langle (S-S_1) \rangle + \tfrac{1}{2}\left[\langle (S-S_1)^2 \rangle - \langle (S-S_1) \rangle^2 \right] + \ldots\ldots \right\},$$

and the possibility of choosing other forms of the center of mass coordinates which differ from those presented in Section VI.3, should also be investigated.

Finally, it should be noted that our view on the dispersion curves of lattice vibrations based on the consideration of Born and Huang[17], as presented in Section I.3, is in fact over simplified. Recently, the details of the phonon dispersion relations have been extensively investigated and much developed. It is now evident that the simple forms of the phonon dispersion relations as presented by Born and Huang does not always provide an adequate physical picture, especially in the region of the electronic phase transitions and at high temperatures. Therefore, some of the simplifying approximations as mentioned in the first section of this chapter will indeed be no longer permissible. It is hoped that in the

future, there will be attempted more rigorous formulations
of the polaron theory that will more realistically take into
account all the known details of the phonon dispersion behav-
iours. This is certainly very important for a still deeper
understanding of the nature of the polaron.