CHAPTER II

THE FROEHLICH HAMILTONIAN

In this chapter, the Froehlich model will be explained in details .The Froehlich Hamiltonian will be derived. In the subsequent section we will present some results that extracted from this Hamiltonian from various works.

When electron in the conduction band (Bloch electron) moving through the polar crystal the ions will be displaced from their equilibrium positions. That is the electron induces the polarization which binds it. This effect can be thought as an electron interact with the phonon field so the Hamiltonian of this system can be seperated as

$$H = H_{electron} + H_{phonon} + H_{interaction} \qquad (2.1)$$

Where the Hamiltonian of the electron should be in the form of kinetic energy, that of the phonon should be a harmonic oscillators type and the interaction must be the form of Coulomb interaction. But, in order to write down the Hamiltonian explicitly, there must be some approximations imposed. The main point is to make this model to be a macroscopic theory. As mentioned previously, the Froehlich model

is the large polaron so the dipole moment due to ions displacment can be approximated to be a dielectric medium.

Furthermore, the very simple model for the crystal that gives rise to this effect is the ionic crystal with two atom per unit cell. The phonons that occur in this type of crystal have six modes of vibration. This can be categorized in two branches, the acoustical and the optical branch which each one has three directions two transverse and one longitude. The acoustic modes are the modes that two types of the ions with different charges vibrate in the same direction where as the optical modes are opposite. So we can see easily that the optical modes give rise to a more strength of the dipole moments and it had been taken into account for the polaron theory. For the acoustic modes, vibration depends on the complicated interaction between neighboring unit cell and the frequencies of vibration depend on the wave vector. Then, in the case of the optical mode which interaction between unit cell are more important, the frequency had been approximated to be a constant. Froehlich simplified further that the magnetic and radiation effects are not to be included so the optical modes can be restricted to only the longitudinal mode. Hence the full name of the polaron may be "the large longitudinal optical polaron".

In the macroscopic dielectric model, there are two types of the polarization vectors(dipole moments per volume. One is the infrared, $\vec{P}_{ir}$, which occurs by displacement of the ions. The other is optical, $\vec{P}_{opt}$,(this is irrelevant to the optical mode of vibration) which comes from the deformation of ions leading to the polarization vectors having free oscillation in the ultraviolet region. The polarization

vector can be approximated to be a continuous function of electron position by above reason. And the total polarization vector becomes

$$\vec{P}_{tot} = \vec{P}_{ir} + \vec{P}_{opt} \qquad (2.2)$$

Since $\vec{P}_{opt}$ depends on it internal structure of the ions and is independent of the dynamics of the system, it gives a constant contribution to the total polarization vector. So we are concern only with $\vec{P}_{ir}$ which can be determined by

$$\vec{P}_{ir} = \vec{P}_{tot} - \vec{P}_{opt} . \qquad (2.3)$$

In static case,

$$\vec{D} = \varepsilon_{\circ}\vec{E} . \qquad (2.4)$$

$\varepsilon_{\circ}$ is the static dielectric constant and

$$\vec{D} = \vec{E} + 4\pi\vec{P}$$

Then the total polarization vector is

$$\vec{P}_{tot} = \frac{1}{4\pi}\left(1 - \frac{1}{\varepsilon_{\circ}}\right)\vec{D} .$$

Similarly, at high frequencies the polarization vector reads

$$\vec{P}_{opt} = \frac{1}{4\pi}\left(1 - \frac{1}{\varepsilon_{\circ}}\right)\vec{D} .$$

Then we have

$$\vec{P}_{ir} = \frac{1}{4\pi}\left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_{*}}\right)\vec{D}.$$ (2.5)

From now on the subscript ir can be suppressed since we are concerned only with this type of polarization vector. We know that the phonon gives rise to this polarization then the polarization vector should have the same equation of motion as that of the harmonic oscillator

$$\ddot{\vec{P}}(\vec{r}) + \omega^2\vec{P}(\vec{r}) = 0.$$ (2.6)

When the electron present, the above equation should be a forced harmonic oscillator with the force proportional to $\vec{D}(\vec{r})$. But our interesting thing is the Lagrangian density

$$L = \frac{\mu}{2}\left[\dot{\vec{P}}^2(\vec{r}) - \omega^2\vec{P}^2\right] + \vec{D}\cdot\vec{P},$$ (2.7)

where μ is to be determined. The last term is the interaction energy density. To derive the Hamiltonian, and by regarding the polarization vector as the generalized coordinates, the conjugate momenta should be found as

$$\vec{p} = \frac{\partial L}{\partial \dot{\vec{P}}} = \mu\dot{\vec{P}}.$$ (2.8)

Then the Hamiltonian becomes

$$H = \int d^3\vec{r} \frac{1}{2} \left[\frac{\dot{\vec{P}}^2(\vec{r})}{\mu} + \mu\omega^2 \vec{P}^2(\vec{r}) - 2\vec{D}(\vec{r})\vec{P}(\vec{r}) \right], \quad (2.9)$$

and the equation of motion are

$$\dot{\vec{P}}(\vec{r}) = \frac{\dot{\vec{p}}}{\mu}, \quad (2.10)$$

$$\vec{p} = -\mu\omega^2 \vec{P} + \vec{D}. \quad (2.11)$$

These two equation gives

$$\ddot{\vec{P}}(\vec{r}) + \omega^2 \vec{P}^2(\vec{r}) = \frac{1}{\mu} \vec{D}(\vec{r}). \quad (2.12)$$

If we consider this equation in the static case which $\dot{\vec{P}} = 0$ leading to the left hand side of equation (2.11) to be vanishes ,then we can determine the value of μ as

$$\mu = \frac{4\pi}{\omega^2} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_\circ} \right). \quad (2.13)$$

Froehlich did not include the magnetic effects, so that this theory can be applied only the slow moving electron and then the displacement field is

$$\nabla \times \vec{D} = 0, \quad (2.14)$$

$$\vec{D}(\vec{r}) = -\nabla \frac{e}{|\vec{r} - \vec{r}_e|} \quad (2.15)$$

where e is the charge of an electron. From equation (2.5) and (2.14), we can write the polarization vector as

$$\vec{P}(\vec{r}) = \frac{1}{4\pi}\nabla\phi(\vec{r}) \,.$$

(2.16)

Then the interaction Hamiltonain

$$H_{int} = -\int d^3\vec{r}\,\vec{D}\cdot\vec{P} = \frac{e}{4\pi}\int d^3\vec{r}\,\nabla_r\frac{1}{\left|\vec{r}-\vec{r}_e\right|}\nabla_r\phi(\vec{r})$$

$$= e\phi\left(r_e\right)$$

(2.17)

and the Hamiltonian of the electron

$$H_e = \frac{\vec{P}_e^2}{2m} = -\frac{1}{2m}\nabla_{r_e}^2 \,.$$

(2.18)

So the total Hamiltonian

$$H = -\frac{\nabla_{r_e}^2}{2m} + \frac{2\pi}{\omega^2}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)^{-1}\int d^3\vec{r}\left(\dot{\vec{P}}^2 + \omega^2\vec{P}^2\right) + \phi\left(r_e\right).$$

(2.19)

And the full form of the Lagrangian is

$$L = \frac{m\dot{\vec{r}}^2}{2} - e\int d^3\vec{r}\,\vec{P}(\vec{r})\left(\nabla\frac{1}{\left|\vec{r}_e - \vec{r}\right|}\right) + \frac{2\pi}{\omega^2}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)^{-1}\int d^3\vec{r}\,\frac{1}{2}\left(\dot{P}^2(\vec{r}) - \omega^2 P^2(\vec{r})\right).$$

(2.20)

The last equation is very important for us since the path integration, the formulation we intend to use, is based on the Lagrangian rather than the Hamiltonian.

So far what we presented is only a classical Hamiltonian and Lagrangian. In order to calculate the energy, we must quantize the Hamiltonian. This can be done by requiring the commutation relation for the position and momentum.

Consider a cube of side L, which is very much larger than the size of the polaron and then we can apply the periodic boundary condition

$$k_i = \frac{2\pi n_i}{L}; \qquad i = 1,2,3,...; \; n_i = int\,eger \qquad (2.21)$$

By introducing the operators (which is the complex field)

$$\vec{B}(\vec{r}) = \sqrt{\frac{\omega\mu}{2}}\left(\vec{P}(\vec{r}) + \frac{i\vec{P}(\vec{r})}{\omega} \right) \qquad (2.22)$$

$$\vec{B}^+(\vec{r}) = \sqrt{\frac{\omega\mu}{2}}\left(\vec{P}(\vec{r}) - \frac{i\vec{P}(\vec{r})}{\omega} \right) \qquad (2.23)$$

And the Fourier series of $\vec{B}(\vec{r})$ is

$$\vec{B}(\vec{r},t) = \frac{1}{\sqrt{V}}\sum_{\vec{k}} \frac{\vec{k}}{|\vec{k}|} \, b_k(t)\exp(i\vec{k}\cdot\vec{r}) \qquad (2.24)$$

and the commutation relation

$$\left[\vec{B}_j(\vec{r}), \vec{B}_j^+(\vec{r}') \right] = \delta(\vec{r} - \vec{r}'). \qquad (2.25)$$

Then we can determine the expression of $\vec{D}(\vec{r})$ as

$$\vec{P}(\vec{r}) = \sqrt{\frac{1}{2\mu\omega V}} \sum_{\vec{k}} \frac{\vec{k}}{|\vec{k}|} \left(b_k^+ e^{-i\vec{k}\cdot\vec{r}} + b_k e^{i\vec{k}\cdot\vec{r}} \right). \tag{2.26}$$

Since $\quad \vec{P} = \dfrac{\nabla\phi(\vec{r})}{4\pi} \quad$ then

$$\phi(\vec{r}) = 4i\pi \sqrt{\frac{1}{2\omega\mu V}} \sum_{k} \frac{1}{|\vec{k}|} \left[b_k^+ e^{-i\vec{k}\cdot\vec{r}} + b_k e^{i\vec{k}\cdot\vec{r}} \right]. \tag{2.27}$$

And the Hamiltonian reads

$$\frac{H}{\omega} = \sum_{k} b_k^+ b_k - \nabla_r^2 + i\sqrt{\frac{4\pi\alpha}{V}}(2m\omega)^{\frac{1}{4}} \sum_{k} \frac{1}{|\vec{k}|} \left(b_k^+ e^{-i\vec{k}\cdot\vec{r}} + H.C. \right), \tag{2.28}$$

where $\quad \alpha = e^2 \sqrt{\dfrac{m}{2\omega}} \left(\dfrac{1}{\varepsilon_\infty} - \dfrac{1}{\varepsilon_s} \right), \tag{2.29}$

is the coupling constant of interaction which has the physical meaning that how much the electron is bound by the polarization field. If this value is larger, the energy will be lower and the effective mass is larger.

Froehlich applied the perturbation method to evaluate the energy from the Hamiltonian (2.28). Within this method the coupling constant α must be small. By imposing the unperturbed wave function as

$$\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V}} |n_1, n_2, \dots \rangle \tag{2.30}$$

and applying the Hamiltonian, the ground state energy is

$$E_{\bullet} = -\alpha\,\omega + \frac{P^2}{2m}\left(1 - \frac{\alpha}{6}\right), \tag{2.31}$$

and we can define the effective mass by the last term as

$$m_{\it eff} = \frac{m}{\left(1 - \dfrac{\alpha}{6}\right)} \tag{2.32}$$

We can see that this expression has a singularity at $\alpha = 6$. Besides, there are many woks concerning the ground state energy and the effective mass of the polaron. Different methods was used to evaluate the intermediate and strong coupling but there is no work can cover all range of the coupling constant except that of Feynman. We will summarize all the results and the methods applied in the table below.

Table 2.1 Summary of the method applied to the polaron problem.

Caculation methods	Self energy	Effective mass	Application range
1. 2nd order perturbation [2].	$E = -\alpha$	$m = (1 - \alpha/6)^{-1}$	Weak coupling
2.Canonical transformation [6].	$E \leq -\alpha$	$m = 1 + \alpha/6$	Weak coupling
3.Canonical transformation [7].	$E \leq -1.26(\alpha/10)^2$ $-1.875(\alpha/10)^3$ $E \leq -1.05\alpha^2$	$m = 1 + \alpha^2/6$ $+2.24(\alpha/10)^2$ $m = 1 + \alpha^2/6$ $+2.24(\alpha/10)^2$	Weak coupling Strong coupling
4 Adiabatic approximation [9].	$E = -0.106\alpha^2$	$m = 0.0208\alpha^2$	Strong coupling
5.Green's functions[12]	$E \leq -\alpha$	$m = 1 + \alpha/6$	Weak coupling
6.Green's function[11]	$E = -0.108\alpha^2 - 3\ln 2$	-	Strong coupling

Table 2.1 (continue)

Caculation methods	Self energy	Effective mass	Application range
7.Path integrals[13]	$E \leq \dfrac{3}{4v}(v-w)^2$ $-\dfrac{\alpha v}{\sqrt{\pi}}\int \dfrac{dxe^{-x}}{F^{\frac{1}{2}}(x)}$	$m = 1 + \dfrac{\alpha v^2}{3\sqrt{\pi}}\int \dfrac{dxe^{-x}}{F^{\frac{1}{2}}(x)}$	All coupling