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## Discrete polarization model of the polaron

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**Abstract.** The energy states of a polaron in the weak-coupling limit were first obtained by Fröhlich, assuming that the polarization of the lattice due to the electron is continuous. In many crystals in which the polaron radius is comparable with the lattice constant, the assumption, however, is not fully justified. To account for the lack of polarization continuity, a polaron model based on the discrete nature of the lattice is proposed in this paper. The model is used for calculating the effect of polarization discreteness on the energy and mass of a polaron which is considered to be near the bottom of the conduction band. The model is also compared with the work of Lepine and Frongillo who follow an alternate approach based on the so-called  $kq$  representation.

### 1. Introduction

Fröhlich [1] was the first to develop the theory of the polaron in crystals in which the electron–phonon interaction is sufficiently weak. The presence of an electron in a polar material induces dipole moments due to the relative movement of the ions of the crystal. If the average extension of the resultant polarization around the electron exceeds the separation between the ions of the lattice, then it is advantageous and mathematically convenient to replace the discrete dipoles by a polarization continuum. The assumption forms the basis of the weak-coupling theory. The polaron in this case is known as a large polaron because the spread of lattice polarization is large compared with the separating distance between the cells of the lattice. The large polarons are generally found in III–V compounds. There are crystals in which the polaron radius is smaller than the lattice constant and the polaron in these crystals is referred to as a small polaron. The earliest work dealing with the small polaron is by Landau and Pekar [2]. In between these two extreme cases there are some perovskites in which the polaron radius is comparable with the lattice constant and the polaron in these crystals is called an intermediate polaron. It is possible to study the properties of these polarons by extending the range of validity of the large-polaron approach which is proposed in this paper, to include the intermediate polaron. This is achieved by maintaining the discrete nature of the lattice. Such a model is developed and used for obtaining the energy states and mass of a polaron near the bottom of the conduction band.

The ground-state energy of the intermediate polaron has recently been studied by Lepine and Frongillo [3] using the  $kq$  approximation [4, 5]. In this approximation the

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positional coordinate of the electron is given by  $q$  which is restricted to the lattice cell and the position of the cell is denoted by  $R$ . The coordinate conjugate to  $R$  is given by  $k$  which describes the translationally invariant motion of the electron. In this representation the interaction of the electron with the neighbouring atoms can be described simultaneously with the translationally invariant motion of the electron in the periodic lattice. The approximation is not particularly easy to follow since the transformation of the Hamiltonian to  $kq$  coordinates prevents its interpretation in terms of the usual coordinates. Using the approximation, Lepine and Frongillo [3] have been able to generalize the Fröhlich Hamiltonian to include the effect of the discrete nature of the polarization. The generalization is, however, not exact since the approximation allows the evaluation of the lower-order correction to the polaron energy due to the discreteness of the lattice but the higher-order corrections are not readily available within the context of the theory. Additionally the theory is critically dependent on the introduction of a cut-off in the integral over the lattice modes since without the cut-off the integral which gives the polaron energy diverges.

In this paper, we propose a discrete lattice model for the polaron in which the electron interacts individually with each ion of the lattice. The interaction leads to changes in the frequencies of the electromagnetic excitations of the crystal. The frequency changes are evaluated and used to calculate the change in the zero-point energy of the crystal. The average interaction energy between the electron and the lattice is given by the shift in the zero-point energy. This approach, which was used earlier by Hawton and Paranjape [6] and Mahanty and Paranjape [7] to determine the self-energy of the electron in a polar crystal, forms the basis of our present calculation. Additionally we treat the interaction between the electron and the lattice as a perturbation and assume that the unperturbed states of the electron are given by plane-wave states. We also consider that the vibrational frequencies of the lattice are undispersed. Our approach is therefore similar to the weak-coupling approach except for the important difference that we assume that the lattice and the associated lattice polarization are discrete rather than continuous. The proposed method allows us to extend the weak-coupling theory to include the effects arising from the discrete nature of the polarization. At this stage we wish to remark that the neglect of dispersion of the optical frequencies in a discrete lattice may appear to be an unreasonable assumption. We have therefore calculated the effect of the phonon dispersion on the polaron energy and its mass separately.

The procedure for obtaining the effect of the discrete polarization on the polaron energy is as follows. When a lattice ion is displaced from its equilibrium position, it acquires a potential energy which is due to its interaction with other ions and in addition also due to its interaction with the mobile electron as is the case in the present paper. Of the two sources the former leads to the vibrational frequency  $\omega_0$  of the ion which we define as the unperturbed frequency. We denote the potential energy of the  $j$ th ion interacting with the mobile electron as  $\delta E(u_j)$  where  $u_j$  is the displacement of the ion from its equilibrium position. Our method, based on quantum mechanics, for obtaining the theoretical expression for the energy  $\delta E(u_j)$  follows the work of Manson and Ritchie [8]. The expression for  $\delta E(u_j)$  is used as a perturbation in the wave equation for the  $j$ th ion. The solution of the wave equation gives the frequency of the ionic motion and also the change in the frequency from its unperturbed value  $\omega_0$ . The total shift in the vibrational energy of the  $N$  lattice ions (i.e. the change in zero-point energy) due to their interaction with the electron is then obtained and equated to the average expectation value of the electron-lattice interaction energy. Since in this approach the individual identity of the ions is maintained, the method is suitable for evaluating the effect of the discrete nature of the lattice on the electron-lattice interaction energy.

The main aim of this paper is to provide a method for obtaining the effect of the discrete nature of the lattice on the polaron energy by calculating the changes in the zero-point energy of the electron–lattice system. Our approach offers an alternative method of accounting for the effect of the discrete lattice on the polaron energy to the approach based on the  $kq$  approximation proposed by Lepine and Frongillo [3]. Although both our method and the method of Lepine and Frongillo give similar results, we believe that our method is more direct. Additionally, for the completeness, we have also obtained the effect of the phonon dispersion on the energy and the mass of the polaron.

### 2. Zero-point energy

Our system consists of a single electron in the conduction band interacting with  $N$  ions of the crystal. The state of the electron is denoted by a plane-wave state with a wavevector  $k_0$ . The ionic states in the absence of electron–lattice interaction are given by  $N$  non-interacting harmonic oscillators. Thus the unperturbed state of our system at zero temperature is described by

$$|k_0, \Pi(0)_n\rangle = |k_0\rangle|0_1\rangle|0_2\rangle \dots |0_n\rangle \dots |0_N\rangle \tag{1}$$

where the first term  $k_0$  denotes the electron state, near the bottom of the conduction band and  $0_n$  denotes the ground state of the  $n$ th oscillator. The excited state is given by the electron in state  $k$  and one ionic oscillator, from the  $N$  oscillators, in the first excited level. Thus the excited level of the system is given by

$$|k, \Pi(\delta_{nm})_n\rangle = |k\rangle|1_m\rangle|0_2\rangle \dots |1_m\rangle \dots |0_n\rangle \dots |0_N\rangle \tag{2}$$

which is  $N$ -fold degenerate.

The potential energy between the electron and the  $j$ th ion is written as  $V(r - R_j)$  where  $r$  is the electron positional coordinate and  $R_j$  is the coordinate of the  $j$ th ion. The equilibrium position of the  $j$ th ion is given by  $R_j^0$  which differs from  $R_j$  by  $u_j$ . If we assume that  $u_j$  is small, then it is possible to develop the potential energy  $V(r - R_j)$  as a power series in  $u_j$  according to

$$V(r - R_j) = V(r - R_j^0) + u_j \cdot \nabla_{R_j^0} V(r - R_j^0) + \dots$$

The potential energy  $\sum_j V(r - R_j^0)$  has the lattice periodicity and, in the effective-mass approximation, its effect on the electron is simply to change its mass  $m$  to the effective mass  $m^*$ .

The potential energy  $\delta E(u_j)$  is defined as the interaction energy between the  $j$ th ion which is displaced from its equilibrium position by amount  $u_j$  and an electron in state  $k_0$ . We obtain the quantity  $\delta E(u_j)$  using the procedure described by Manson and Ritchie [8] and the definition

$$\Delta E = \int \langle u_j | 0_j \rangle \delta E(u_j) \langle 0_j | u_j \rangle du_j \tag{3}$$

where  $\Delta E$  is the average interaction energy between the electron and the lattice and is given by the second-order perturbation theory:

$$\Delta E = \sum_{k,m} \frac{|\langle k_0, \Pi(0)_n | H' | k, \Pi(\delta_{nm})_n \rangle|^2}{E_{k_0} - E_k - \hbar\omega_0} \tag{4}$$

where the interaction Hamiltonian  $H'$  is given by

$$H' = \sum_i H'_i \quad H'_i = u_i \cdot \nabla_{R_i^0} V(r - R_i^0). \tag{5}$$

The unperturbed energy of the electron is given by  $E_k = \hbar^2 k^2 / 2m^*$ . For our purposes it

is sufficient to consider only the first excited state of the ionic oscillators. Comparing equations (3) and (4) and following Manson and Ritchie [8] allows us to write

$$\delta E(u_j) = \sum_k \frac{\langle k_0 | H_j'(u_j) | k \rangle \langle k, 1_j | H_j'(u_j) | k_{q_0}, 0_j \rangle \langle u_j | 1_j \rangle}{E_{k_0} - E_k - \hbar\omega_0} \langle u_j | 0_j \rangle \quad (6)$$

If we now develop the bare potential energy  $V(r - R_j^0)$  between the ion at  $R_j^0$  and the electron at  $r$  in terms of a Fourier series as follows:

$$V(r - R_j^0) = \sum_q V(q) \exp[iq \cdot (r - R_j^0)] \quad (7)$$

then it is possible to write

$$H_j' = - \sum_q u_j \cdot (iq) V(q) \exp[iq \cdot (r - R_j^0)]. \quad (8)$$

To obtain  $\delta E(u_j)$  in equation (6) we need various matrix elements and oscillator wavefunctions. They can be found in any standard textbook on quantum mechanics [9]. The results are given below:

$$\langle u_j | 0_j \rangle = (1/2\pi r_p^2)^{3/4} \exp(-u_j^2/4r_p^2) \quad (9)$$

$$\langle u_j | 1_j \rangle = [(2)^{1/2}/\pi^{3/4}] (1/2r_p^2)^{5/4} u_j \exp(-u_j^2/4r_p^2) \cos \theta \quad (10)$$

$$\langle 0_j | q \cdot u_j | 1_j \rangle = q r_p \quad (11)$$

and finally

$$\langle k_0 | H_j'(u_j) | k \rangle = \sum_q u_j \cdot (-iq) V(q) \exp(-iq \cdot R_j^0) \delta_{k, k_0 - q}. \quad (12)$$

In equations (9)–(11) we have substituted  $r_p$  for  $(\hbar/2m^* \omega_0)^{1/2}$  which is known to be the polaron radius. In equation (8) the angle  $\theta$  is in between  $u_j$  and  $q$ . Substituting equations (8)–(12) into (6) we get

$$\delta E(u_j) = \sum_q \frac{|V(q)|^2 (q \cdot u_j)^2}{E_{k_0} - E_{k_0 - q} - \hbar\omega_0}. \quad (13)$$

We now set up the Schrödinger equation for the  $j$ th ion using equation (13):

$$[(-\hbar^2/2M)\nabla^2 + (M\omega_0^2/2)u_j \cdot u_j + \delta E(u_j)] \langle u_j | 0_j \rangle = \mathbb{E}_j \langle u_j | 0_j \rangle \quad (14)$$

where  $\mathbb{E}_j$  is the perturbed ground-state energy of the  $j$ th oscillator. The second term on the right-hand side of equation (14) is the potential energy of the oscillator in the absence of the electron and the third term gives the change in the potential energy due to the presence of the electron in state  $k_0$ . Substituting (13) into (14) and solving for  $\mathbb{E}_j$  leads to

$$\mathbb{E}_j = \frac{1}{2}\hbar \left( \omega_0^2 - \frac{2}{M\hbar} \sum_q \frac{q^2 |V(q)|^2}{E_{k_0 - q} - E_{k_0} + \hbar\omega_0} \right)^{1/2}. \quad (15)$$

On the assumption that there are  $N$  oscillators, the shift in the zero-point energy of the lattice is given by

$$\Delta E = - \frac{N\hbar}{2\mu\omega_0} \sum_q \frac{q^2 |V(q)|^2}{E_{k_0 - q} - E_{k_0} + \hbar\omega_0} \quad (16)$$

where we have replaced the ion mass by the reduced mass  $\mu$ . The wavevector  $q$  is defined

in the development of the electron-ion interaction as given by equation (7). Its range covers the entire reciprocal space, while the energy  $E$  is defined in a single band. Therefore the  $k$ -values occurring in the energy  $E$  are restricted to the first Brillouin zone. We restrict all the wavevectors occurring in equation (16) to the first Brillouin zone by writing equation (16) as follows:

$$\Delta E = - \frac{N\hbar}{2\mu\omega_0} \sum_{q,G} \frac{(q+G)^2 |V(q+G)|^2}{(E_{k_0-q} - E_{k_0} + \hbar\omega_0)} \tag{17}$$

where  $G$  are the reciprocal lattice vectors. The effect of the lattice structure is included in the interaction energy  $\Delta E$  through the reciprocal lattice vectors. We shall evaluate the energy given by equation (17) in the following section.

### 3. Calculation

#### 3.1. Effect of the discrete lattice

The interaction energy as given by equation (17) is obtained directly without using the Fröhlich Hamiltonian and assuming the discrete nature of the lattice. The effect of the discrete lattice is included through the reciprocal lattice vectors and by the fact that the summation over  $q$  is restricted to the first Brillouin zone. It is important to realize that the expression for  $\Delta E$  as given by equation (17) is independent of a specific form of the bare potential  $V(r - R_j^0)$  between the electron and the  $j$ th lattice ion. The flexibility offered by equation (17) in the selection of the potential energy  $V(r - R_j^0)$  and in the selection of the appropriate crystal structure makes it particularly useful for the study of the structural effects of the lattice on the polaron energy. We select a relatively simple form of the potential energy between the electron at  $r$  and the  $j$ th lattice ion, according to

$$V(r) = (\pm)e^2/\epsilon_\infty |r - R_j^0| \tag{18}$$

and its Fourier component as

$$V(q) = (\pm) 4\pi e^2/\epsilon_\infty \Omega q^2 \tag{19}$$

where  $\epsilon_\infty$  is the high-frequency dielectric constant,  $\Omega$  is the crystal volume and the positive or negative signs arise depending on the charge of the ion. We now define the well known Fröhlich constant  $\alpha$  according to

$$\alpha = (e^2/\hbar)(m/2\hbar\omega_0)^{1/2}(\epsilon_\infty^{-1} - \epsilon_0^{-1}) \tag{20}$$

and express the relation between the zero- and high-frequency dielectric constants and the optical mode frequency  $\omega_0$  of the polar crystal according to [4, 8]

$$4\pi e^2 N/M\epsilon_\infty \Omega = (\omega_0^2/\epsilon_0)(\epsilon_0 - \epsilon_\infty). \tag{21}$$

We now make use of equations (18)–(21) for obtaining the interaction energy  $\Delta E$  as given by equation (17). We assume that the Brillouin zone is spherical so that the maximum value  $|q|$  is given by  $q_m$ , in all directions.

$$\Delta E = - \frac{(\alpha\hbar\omega_0)}{(2\pi)^2} \left(\frac{2m}{\hbar}\right) \left(\frac{2\hbar\omega_0}{m}\right)^{1/2} \sum_n \int \frac{q^2 dq \sin\theta d\theta d\varphi}{(q+G_n)^2 (q^2 + r_p^{-2})} \left(1 - \frac{2k_0 q}{q^2 + r_p^{-2}} \cos\gamma\right)^{-1} \tag{22}$$

where  $\gamma$  is the angle between  $k_0$  and  $q$ , and the angles  $\theta$  and  $\varphi$  are the polar angles made

by  $q$  with  $G_n$  which is the polar axis. If we define  $\theta_n$  and  $\varphi_n$  as the polar angles of the vector  $k_0$  made with the polar axis  $G_n$ , then the trigonometric consideration gives

$$\cos \gamma = \cos \theta \cos \theta_n + \sin \theta \sin \theta_n \cos(\varphi - \varphi_n). \quad (23)$$

Expanding equation (22) in powers of  $k_0$ , and retaining terms up to  $k_0^2$  the average interaction energy  $\Delta E$  is then given by

$$\Delta E = -\frac{(\alpha \hbar \omega_0)}{(2\pi)^2} \left(\frac{2m}{\hbar}\right) \left(\frac{2\hbar \omega_0}{m}\right)^{1/2} \sum_n \int_0^{q_m} \frac{q^2 dq \sin \theta d\theta d\varphi}{(q^2 + G_n^2 + 2qG_n \cos \theta)} \\ \times \frac{1}{q^2 + r_p^{-2}} \left(1 + \frac{4k_0^2 q^2}{(q^2 + r_p^{-2})^2} \cos^2 \gamma\right). \quad (24)$$

we now write  $\Delta E$  as a sum of two terms:  $\Delta E = \Delta E_0 + \Delta E_1$  where  $\Delta E_0$  corresponds to putting  $k_0 = 0$  in (24) so that it represents the shift in the conduction band edge.  $\Delta E_1$  arises from the term  $[4k_0^2 q^2 / (q^2 + r_p^{-2})^2] \cos^2 \gamma$  in equation (24) and gives the dynamic effects of the mobile electron on  $\Delta E$ . On integration we get

$$\Delta E_0 = -\alpha \hbar \omega_0 \left( \frac{2}{\pi} \tan^{-1}(q_m r_p) + \frac{2}{\pi} \sum_n' \frac{q_m}{r_p G_n^2} [1 - (r_p q_m)^{-1} \tan^{-1}(q_m r_p)] \right) \quad (25)$$

where in the first term we have separated out the  $G = 0$  term and the second term contains the effect of the lattice structure through  $G_n$  for  $n$  greater than zero. Furthermore in obtaining equation (25) we have expanded equation (24) in powers of  $q_m/|G|$  and retained terms up to  $(q_m/|G|)^2$ . For a more realistic calculation in which the actual shape of the Brillouin zone is needed, one must resort to numerical integration of (24). Similarly we get

$$\Delta E_1 = -\frac{\alpha \hbar^2 k_0^2}{6m\pi} \left\{ \tan^{-1}(r_p q_m) + \frac{q_m r_p (q_m^2 r_p^2 - 1)}{(1 + q_m^2 r_p^2)^2} + \sum_n' \frac{12}{r_p^2 G_n^2} \left[ \frac{1}{4} \tan^{-1}(q_m r_p) \right. \right. \\ \left. \left. - \frac{5}{12} \frac{q_m r_p}{(1 + r_p^2 q_m^2)} + \frac{q_m r_p}{6(1 + r_p^2 q_m^2)^2} + \frac{q_m}{r_p G_n^2} \left( \frac{8}{3} \cos^2 \theta_n + \frac{16}{3} \sin^2 \theta_n - \frac{8}{3} \right) \right. \right. \\ \left. \left. \times \left( 1 + \frac{9}{8(q_m^2 r_p^2 + 1)} - \frac{1}{4(q_m^2 r_p^2 + 1)^2} - \frac{15}{8r_p q_m} \tan^{-1}(r_p q_m) \right) \right] \right\}. \quad (26)$$

The approximate expression for  $\Delta E$  in the limit  $r_p q_m$  approaching infinity is given as

$$\Delta E = -\alpha \hbar \omega_0 \left\{ 1 - \frac{2}{r_p q_m \pi} \left[ 1 - \sum_n' \left( \frac{q_m}{G_n} \right)^2 \right] \right\} - \frac{\alpha \hbar^2 k_0^2}{6m\pi} \left( \frac{\pi}{2} + \sum_n' \frac{3\pi}{2r_p^2 G_n^2} \right) \quad (27)$$

where we have retained terms up to  $1/r_p q_m$ . If we neglect terms  $(r_p q_m)^{-1}$  and  $(r_p G_n)^{-1}$  in equation (27), then the expression reduces to the well known result valid for the large-polaron case, i.e.

$$\Delta E = -\alpha \hbar \omega_0 - \alpha \hbar^2 k_0^2 / 12m. \quad (28)$$

The energy  $\varepsilon(k_0)$  of the electron consisting of the unperturbed and perturbed parts can be written as

$$\varepsilon(k_0) = \frac{\hbar^2 k_0^2}{2m} - \alpha \hbar \omega_0 \left\{ 1 - \frac{2}{r_p q_m \pi} \left[ 1 - \sum_n' \left( \frac{q_m}{G_n} \right)^2 \right] \right\} - \frac{\alpha \hbar^2 k_0^2}{6m\pi} \left( \frac{\pi}{2} + \sum_n' \frac{3\pi}{2r_p^2 G_n^2} \right) \quad (29)$$

where we have used equation (27) for  $\Delta E$  and  $\varepsilon(k_0) = E_{k_0} + \Delta E$ .

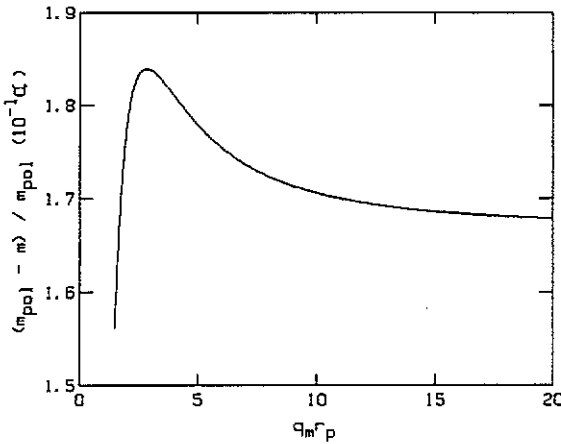


Figure 1. Variation in  $(m_{\text{pol}} - m)/m_{\text{pol}}$  as a function of  $r_p q_m$ .

The expression for polaron mass  $m_{\text{pol}}$  can be obtained if we define

$$1/m_{\text{pol}} = (1/\hbar^2) [\partial^2 \epsilon(k_0)/\partial k_0^2]. \tag{30}$$

Using the definition (30) and equation (29) we get

$$\frac{1}{m_{\text{pol}}} = \frac{1}{m} \left( 1 - \frac{\alpha}{6} - \alpha \sum_n' \frac{1}{2r_p^2 G_n^2} \right). \tag{31}$$

If we restrict ourselves to the smallest reciprocal lattice vectors  $G_1$  and write  $G_1$  in terms of the lattice constant  $a$  according to  $G_1 = 2\pi/a$ , then the expression for the polaron mass for a crystal with cubic symmetry becomes

$$1/m_{\text{pol}} = (1/m) [1 - \alpha/6 - \alpha(3/4\pi^2)(a^2/r_p^2)]. \tag{32}$$

We conclude from (32) that, if  $a/r_p$  is comparable with unity, the effect of the discrete nature of the polarization on the polaron mass is not negligible.

For numerical estimates we obtain a more exact result for the polaron mass by making use of equations (25), (26), (29) and (30). We also consider a cubic lattice and take into account only the smallest reciprocal lattice vectors, i.e. the  $G_1$ -values. With these assumptions the effect of the angular dependence is eliminated and the expression for the polaron mass can be written as

$$\begin{aligned} (m_{\text{pol}} - m)/m_{\text{pol}}\alpha = & (1/3\pi) \{ \tan^{-1}(r_p q_m) + q_m r_p (q_m^2 r_p^2 - 1)/(1 + r_p^2 q_m^2)^2 \\ & + (3/r_p^2 q_m^2) \{ \frac{3}{8} \tan^{-1}(r_p q_m) \\ & - \frac{5}{8} q_m r_p / (1 + r_p^2 q_m^2) + q_m r_p / (1 + r_p^2 q_m^2)^2 + (\frac{3}{8}/r_p q_m) [1 + 9/8(1 + q_m^2 r_p^2) \\ & - 1/4(1 + r_p^2 q_m^2)^2 - (15/8 r_p q_m) \tan^{-1}(r_p q_m)] \} \}. \end{aligned} \tag{33}$$

Equation (33), shown graphically in figure 1, gives the polaron mass in terms of  $r_p q_m$ . if  $r_p q_m$  approaches infinity, the polaron radius is very much larger than the interionic distance and the right-hand side of equation (33) approaches the asymptotic value equal to 0.1666 which gives the well known result for the polaron mass in the large-polaron



limit. We shall use equation (33) as shown in figure 1 to estimate the value of the polaron mass for specific compounds in the following section.

### 3.2. Effect of the phonon dispersion

To consider the effect of lattice dispersion on the polaron energy and the polaron mass we write  $\Delta E$  as follows:

$$\Delta E = -\frac{N\hbar}{2\mu} \sum_q \frac{q^2 |V(q)|^2}{\omega(q) [E_{k_0-q} - E_{k_0} + \hbar\omega(q)]} \quad (34)$$

Equation (34) is similar to equation (17) except for the differences that the phonon frequency is now assumed to depend on the wavevector  $q$  and the effect of reciprocal lattice vectors of magnitude greater than zero are neglected. The summation over  $q$  is, as before, restricted to the first Brillouin zone. We now assume that the optical phonon frequency depends on  $q$  as follows:

$$\omega(q) = \omega_0 - \delta(q/q_m)^2 \quad (35)$$

where  $\delta = \omega_0 - \omega'$  and  $\omega'$  is the optical phonon frequency at  $q = q_m$ .  $\delta$  represents the frequency spread between  $\omega_0$  at zero  $q$  and  $\omega'$ . Usually  $\delta$  is positive. We now substitute equations (19), (20), (21) and (35) into equation (34) and develop the resulting equation in powers of  $k_0$ . Retaining terms up to  $k_0^2$  and performing the integration over  $q$ , we get expressions similar to those given by equations (25) and (26). Retaining the same notation as used in calculating the effect of the discrete lattice in section 3.1, we write  $\Delta E = \Delta E_0 + \Delta E_1$  where

$$\begin{aligned} \Delta E_1 = & -(\alpha\hbar^2 k_0^2 / 6m\pi) \{ \tan^{-1}(x^2 - \beta)^{1/2} [(x^4 - 4x^2\beta - 8\beta^2)/x^3(x^2 - \beta)^{1/2}] \\ & + [x^4 - x^2(1 + 5\beta) + 4\beta^2 - 4\beta]/x(1 + x^2 - \beta)^2 \\ & - (4\beta^{3/2}/x^3) \log_e[(1 - \beta^{1/2})/(1 + \beta^{1/2})] \}. \end{aligned} \quad (36)$$

Here we have used  $x = r_p q_m$  and  $\beta = \delta/\omega_0$ . An expression for  $\Delta E_0$  can also be written, but we do not do so for brevity. We note that equation (36) gives the dynamical part of the interaction energy due to the phonon dispersion and contains the first-order effect due to the discrete lattice since the  $q$ -values are restricted to the first Brillouin zone. The expression does not contain contributions arising from the higher reciprocal lattice vectors beyond the zeroth reciprocal vector. Using equation (30) we can write the expression for the polaron mass as follows:

$$\begin{aligned} (m_{\text{pol}} - m)/m_{\text{pol}}\alpha = & (1/3\pi) \{ \tan^{-1}(x^2 - \beta) [(x^4 + 4\beta x^2 - 8\beta^2)/x^3(x^2 - \beta)^{1/2}] \\ & + [x^4 - x^2(1 + 5\beta) + 4\beta^2 - 4\beta]/x(1 + x^2 - \beta)^2 \\ & - (4\beta^{3/4}/x^3) \log_e[(1 - \beta^{1/2})/(1 + \beta^{1/2})] \}. \end{aligned} \quad (37)$$

If we put  $\beta = 0$ , then the effect of phonon dispersion is removed from equation (37) and the right-hand side of the equation gives the effect of the discrete lattice as given by the first two terms in the open-face square brackets (II) in equations (33). We shall use

equation (37) to evaluate the effect of the phonon dispersion on the polaron mass of specific compounds in the following section.

#### 4. Discussion and results

We have obtained in this paper an expression for the polaron energy which is valid for the polaron whose radius is larger than but comparable with the lattice constant  $a$ . The ground-state energy of the polaron is given by equation (25) in which the effect of the discrete nature of lattice polarization is given by the second term while the first term gives the Frohlich result for the large polaron. If we set  $q_m = \pi/a$  and  $G_1 = 2\pi/a$  with six  $G_1$ -vectors, then neglecting the contributions of  $G$ -vectors higher in magnitude than  $G_1$  and expanding the energy expression in powers of  $q_m r_p$ , we get

$$\Delta E_0 = -\alpha \hbar \omega_0 (1 + a/\pi^2 r_p + \dots). \quad (38)$$

When  $a/r_p$  approaches zero, the second term in (38) decreases to zero and the first term gives the Fröhlich result for the weak-coupling polaron. When  $r_p$  is comparable with  $a$ , we find that the effect of the discreteness on  $\Delta E_0$  can be as large as 10%. The expression is similar in form to the expression derived by Lepine and Frongillo [3] using  $kq$  representation. However since the work of the earlier researchers is based on the use of a cut-off, the difference between the numerical constant of our result and that of Lepine and Frongillo [3] is not too surprising.

We now consider the term  $\Delta E_1$  which contains the effect of the electron motion on the polaron energy through the term  $k_0$  and also the effect of the electron-lattice interaction on the polaron mass. Equation (33) gives the change in the polaron mass due to the discrete nature of the lattice, and equation (36) gives the effect of the phonon dispersion on the polaron mass.

To discuss the effects of lattice discreteness on the polaron mass we consider potassium chloride as an example. For this material [3] the Fröhlich coupling constant  $\alpha = 3.44$  and  $r_p q_m = 9.05$ . Using these values and figure 1, we can obtain the value of  $\Delta m_{\text{pol}}(r_p q_m = 9.05)$ . If we assume that the lattice is continuous (i.e. neglecting the discreteness of the lattice) the change in the polaron mass for this case is given by  $\Delta m_{\text{pol}}(r_p q_m = \infty)$  and is obtained from figure 1 by using  $r_p q_m = \infty$ . For KCl the ratio

$$[\Delta m_{\text{pol}}(x = 9.05)/\Delta m_{\text{pol}}(x = \infty)] = 1.077$$

where we have written  $x = r_p q_m$ . For RbCl, we have  $\alpha = 3.81$  and  $r_p q_m = 9.44$ . Again, using figure 1 we obtain the value

$$[\Delta m_{\text{pol}}(x = 9.44)/\Delta m_{\text{pol}}(x = \infty)] = 1.087.$$

For NaCl,  $\alpha = 4.86$ ,  $r_p q_m = 5.96$  and the ratio

$$[\Delta m_{\text{pol}}(x = 5.96)/\Delta m_{\text{pol}}(x = \infty)] = 1.37.$$

For NaCl the band mass is not known and the bare mass is used in the evaluation of the parameters. This overestimates the value of  $\alpha$  and the effect of the discreteness. Hence the results for NaCl are not reliable, although it gives rather a large effect arising from discreteness of the lattice. All parameter values used are given in [10].

We now turn our attention to equation (37) which gives the effect of the phonon dispersion on the polaron mass. The equation also contains the lowest-order effect of the discreteness of the lattice on the polaron mass. The examination of equation (37) clearly shows that the effect of phonon dispersion which is included through the term  $\beta$  is small if  $r_p q_m$  is large and if  $\beta$  is small. For moderately small values of  $r_p q_m$  the effect of the phonon dispersion can be significant. For the materials considered earlier while discussing the effect of lattice discreteness, we find that the effect of the phonon dispersion is not negligible but it is much less than the effect of the lattice discreteness.

Equation (37) gives the change in the polaron mass if phonon dispersion is in the form given by equation (34) and if the parameter  $\beta$  is given. The equation also contains the effect of the discrete lattice up to the first order through the parameter  $x = r_p q_m$ . For KCl we estimate [11] the average value of  $\beta = 0.25$  and as before  $\alpha = 3.44$  and  $x = 9.05$ . Using equation (37) we get

$$[\Delta m_{\text{pol}}(\beta = 0.25)/\Delta m_{\text{pol}}(\beta = 0)] = 1.028.$$

For RbCl,  $\beta = 0.23$  and as before  $\alpha = 3.81$  and  $x = 9.44$ . The change in the polaron mass due to phonon dispersion is

$$[\Delta m_{\text{pol}}(\beta = 0.23)/\Delta m_{\text{pol}}(\beta = 0)] = 1.03.$$

From the numerical estimates of the effect of the lattice discreteness and of the phonon dispersion on the polaron mass, we conclude that the effect of the lattice discreteness is larger than the effect of the phonon dispersion. The effect of the phonon dispersion is, however, not negligible. The combined effects of the two could be sufficiently large and measurable.

A very comprehensive review on the subject of experimental measurements of the polaron mass is given by Hodby [12]. It is possible to obtain the polaron mass quite accurately using cyclotron resonance measurements, the accuracy being limited by the purity of the sample. Some of the results obtained in this work can possibly be observed if measurements of the polaron mass are made in crystals which are subjected to strong linear or hydrostatic pressures. Such pressures could cause a change in the lattice constant and hence the polaron mass.

Finally, we wish to remark on a feature in equation (26). It gives the self-energy of the electron which is direction dependent with respect to the reciprocal lattice vectors. The effect is quite small. It is eliminated in the case of cubic crystals. It is not very likely that the effect could be detected by measuring the polaron mass since the band mass of the electron has its own anisotropic character and the anisotropy predicted in this work is expected to be much smaller than the natural anisotropy of the band mass owing to the static lattice.

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