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Ground state energy of a bound polaron.

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The Ground State Energy Of A Bound Polaron

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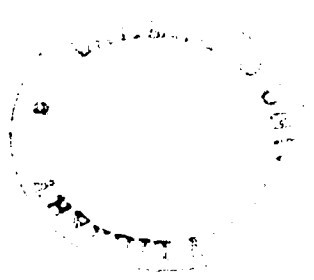A Thesis Submitted In Candidature for the

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CHAPTER   I

Introduction

The motion of an electron in an ionic crystal has been of considerable interest since early 1930's - firstly because of its relevance to the applied physics of semi-conductors and secondly because it provides a simple model for the study of interaction between a particle and a quantum field. It is the first problem in Solid State Physics to which methods of quantum field theory have been applied.

The polaron problem is concerned with the motion of a slow electron in a polar material. The electron as it moves through the crystal disturbs the lattice in its neighbourhood and thereby creates a polarization field. The field in turn acts on the electron and changes its energy. The electron together with its accompanying polarization field can be thought of as a quasi particle called "polaron". The Hamiltonian H for such a system can be written as

$$H = H_{lat} + H_{el} + H_{int}$$

(1.1)

where H_{lat} is the Hamiltonian corresponding to the energy of the lattice, H_{el} is the kinetic and potential energy of an electron in the static lattice and H_{int} represents the interaction between

the electron and the lattice. Exact calculation of the eigen states

with corresponding eigen energies for the Hamiltonian H has not

been possible so far. Different approaches to solve the problem

have been used depending on the strength of interaction. Pekar

who first calculated the polaron eigen states considered a special

case in which the interaction is assumed to be so strong that the essen-

tial properties of a stationary polaron are described by a localized

electron moving in its own polarization field. Fröhlich, who was

the first to employ the methods of quantum field theory to this

problem, considered the weak interaction case and used the pertur-

bation theory to calculate the polaron energy states. The intermediate

coupling case has also received considerable attention in literature.

All the works referred to so far deal with the motion of an electron

suitably affected by its polarization field. In many practical

situations, however, an electron in a polar crystal may be bound

to an impurity center. In this case the electron motion is influenced

not only by the impurity but also by its own polarization field. We

thus have a situation for the electron state which can be described

as a "bound polaron". This quasi particle is very similar to the

polaron described earlier and the Hamiltonian describing the bound

polaron is similar to Eqn (1.1) apart from an additional term due

to the potential energy of an electron in the presence of an impurity

atom. Platzman was the first to calculate the energy states of a

bound polaron and since then several papers have appeared in the

literature. The present thesis is concerned with the calculation of the ground state energy of a bound polaron. Our approach to this calculation is based on the assumption of weak electron lattice interaction so that the perturbation theory is assumed to hold. The detailed calculations are given in Chapter III.

In the following chapter we shall give a brief introduction to the development of the Hamiltonian for the electron-lattice interaction. The derivation is based on the work of Fröhlich and we shall show that the Hamiltonian for a polaron can be written as

$$H = -\frac{\hbar^2}{2m} \nabla^2_{el} + \sum_q \hbar\omega \left(b^\dagger_q b_q + \frac{1}{2} \right)$$
$$+ \frac{iU}{V^{1/2}} \sum_q \frac{1}{|q|} \left[b^\dagger_q e^{-iq\cdot x} - b_q e^{iq\cdot x} \right] \tag{1.2}$$

where

$$U = \hbar\omega \left(4\pi\alpha \right)^{1/2} \left(\hbar/2m\omega \right)^{1/4} \tag{1.3}$$

and

$$\alpha = \frac{e^2}{\hbar} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right] \left(m/2\hbar\omega \right)^{1/2} \tag{1.4}$$

The first term in Eqn (1.2) is the kinetic energy of an electron in the periodic lattice with m as its effective mass. The second term describes the lattice energy in terms of the usual creation and

destruction operators b_q^+ and b_q for the lattice modes of wave vector q . The last term is the electron lattice interaction. The quantity α is the coupling constant for the electron lattice interaction and is expressed in Eqn (1.4) in terms of ω_q the frequency of optical polar modes, ϵ_∞ and ϵ_0 the high and low frequency dielectric constants. Starting from the Hamiltonian (1.2) we shall calculate the energy of an electron using perturbation theory and show that for weak electron-lattice interaction the polaron mass m^* is related to the band mass m by the relation

$$m^* = m \left(1 + \frac{\alpha}{6} \right)$$

(1.5)

For $\alpha = 0$, i.e., neglecting the effect of electron-lattice interaction, the polaron mass is equal to band mass as is expected.

In Chapter III we deal with the bound polaron problem and give the calculation of the ground state energy of a polaron bound to a coulombic impurity. We shall see that the method first introduced by Platzman gives the shift in energy ΔE due to the interaction of a bound electron with its accompanying polarization fields in the following form:

$$\Delta E = -\alpha \hbar \omega \left(1 + \frac{\beta^2}{6} + \frac{\beta^4}{24} + \cdots \right)$$

(1.6)

where $\beta^2 = -E_1/\hbar\omega$ is the ratio of the unperturbed ground state energy to the energy of the optical modes of the lattice. The

result as given by Eqn (1.6), according to Platzman, holds only
when

$$\beta^2 << 1.$$

(1.7)

Platzman obtained the expression for ΔE given in Eqn (1.6) by
employing an expansion procedure which requires the validity of
the condition (1.7). Even though the condition (1.7) may be sat-
isfied for many polar crystals with suitable donor impurities,
in practice, situations may arise in which case this condition
may not hold. In this thesis a new approach for calculating
is proposed. Even though our method is accurate when condition
(1.7) is satisfied, it may provide a reasonable estimate of
even in situation when $\beta^2 > 1$. We shall show that our method
gives the following expression for ΔE in the following form:

$$\Delta E = -\alpha \hbar w \left\{ \frac{8}{3} (1 + \beta^2) \left[(3/8) - (\beta^2/2) + \beta^4 (1 - \sqrt{\beta^2/1+\beta^2}) \right] \right.$$
$$\left. + \beta^2 (1 + \beta^2)^{-3/2} - \frac{\beta^4}{3} (1 + \beta^2)^{-5/2} \right\}$$

(1.8)

If $\beta^2 << 1$ then the right hand of Eqn (1.8) may be expanded in terms
of β and if terms of to the 4th power in β are re ained then
in Eqn (1.8) reduces exactly to Eqn (1.6) - a result obtained by
Platzman. If β is allowed to go to infinity then ΔE in (1.8)
reduces to zero and one may conclude that the polarization field

is unable to follow the electronic motion in this limit - a result which is expected in a strongly bound electronic state. Our result for $\triangle E$ therefore tends to approach the correct result for the two extreme values for β and one would reasonably expect that for the intermediate values of β our result would provide a reasonable extimate for $\triangle E$.

C H A P T E R   I I

The Free Polaron

1   Derivation of The Hamiltonian

The derivation of the Hamiltonian can be found in many advanced text books on Solid State Physics. In this chapter we therefore only give important steps in its development following the original papers by Fröhlich.

Our system consists of a single electron interacting with the optical modes of the lattice. If only long wavelengths for the lattice modes are to be considered, then the energy of the lattice and the interaction energy of an electron and the lattice can be studied in terms of the polarization field $P_{Tot}(x)$. The field $P_{tot}(x)$ is composed of the optical $P_{opt}(x)$ and infrared $P(x)$ components, so that:

$$P_{tot}(x) = P_{opt}(x) + P(x)$$

(2.1)

The optical component is important only if magnetic and radiation effects are not being considered and therefore $P(x)$ is considered of little relevence in this thesis.

Using the definition for the dielectric constant

$$D = \epsilon E$$

(2.2)

where $\underset{\sim}{D}$ and $\underset{\sim}{E}$ are related by

$$\underset{\sim}{D} = \underset{\sim}{E} + 4\pi \underset{\sim}{P}_{tot}$$

(2.3)

so that we may write

$$\underset{\sim}{P}_{tot}(\lambda) = \frac{1}{4\pi}\left(1 - \frac{1}{\epsilon}\right)\underset{\sim}{D}(\lambda)$$

(2.4)

If the high frequency value of the dielectric constant is used in (2.4) we get

$$\underset{\sim}{P}_{opt}(\lambda) = \frac{1}{4\pi}\left(1 + \frac{1}{\epsilon_\infty}\right)\underset{\sim}{D}(\lambda)$$

(2.5)

Combining Eqns (2.1) (2.4) and (2.5) we get

$$\underset{\sim}{P}(\lambda) = \frac{1}{4\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right)\underset{\sim}{D}(\lambda) = \frac{1}{4\pi}\frac{1}{\bar{\epsilon}}\underset{\sim}{D}(\lambda)$$

(2.6).

The equation of motion for $\underset{\sim}{P}(\lambda)$ in absence of a polarizing source is a simple harmonic motion at frequency ω corresponding to the polar optical mode of the lattice, and is given by

$$\underset{\sim}{\ddot{P}}(\lambda) + \omega^2 \underset{\sim}{P}(\lambda) = 0$$

(2.7)

If a polarizing source - (an electron) is present then Eqn. (2.7) will be modified. We shall consider these modifications later in this section.

We shall now develop a Lagrangian for our system so that we may obtain the required Hamiltonian and also the equation of motion for $P(\underset{\sim}{r})$.

Now since $D(\underset{\sim}{r})$ is the external field and $P(\underset{\sim}{r})$ is the effective polarization field the interaction energy density is given by $-D(\underset{\sim}{r}) \cdot P(\underset{\sim}{r})$. We may then write the Lagrangian of our system as:

$$L = \frac{\mu}{2} \int \left[\dot{P}^2(\underset{\sim}{r}) - \omega^2 P^2(\underset{\sim}{r}) \right] d^3r$$

$$+ \frac{1}{2} m \, \dot{r}_{elc}^2$$

$$+ \int D(\underset{\sim}{r}) \cdot P(\underset{\sim}{r}) \, d^3r$$

$$\tag{2.8}$$

where μ is introduced as a parameter to be determined and r_{elc} is the position coordinate of the electron. Since $D(\underset{\sim}{r})$ is the field produced at $\underset{\sim}{r}$ by an electron at r_{elc} we may write

$$D(\underset{\sim}{r}, r_{elc}) = - \nabla_r \frac{e}{|\underset{\sim}{r} - r_{el}|}$$

$$\tag{2.9}$$

and

$$\nabla \cdot D = 4\pi e \, \delta(\underset{\sim}{r} - r_{elc})$$

$$\tag{2.10}$$

Hamiltonian can be obtained from the Lagrangian given by Eqn (2.8) and may be expressed as

$$H = \int d^3r \left[\frac{\mu}{2} \left\{ \dot{P}^2(r) + \omega^2 P^2(r) \right\} - D(r) \cdot P(r) \right] + \frac{1}{2} m \dot{r}^2_{el}$$

(2.11)

where the generalized coordinates are $P(r)$ and $\mu \dot{P}(r)$ and $\mu \dot{P}(r)$ is the conjugate generalized momenta. The equation of motion for $P(r)$ can be obtained from the Hamiltonian in Eqn (2.11) using the standard procedure to give

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

(2.12)

which is consistant with (2.7) in the absence of a polarizing source, i.e., an electron. We may use Eqn. (2.6) and consider Eqn. (2.12) in the static limit, i.e., $\ddot{P} = 0$ so that the unknown parameter μ may be determined. It therefore follows that:

$$\mu = \frac{4\pi \bar{\epsilon}}{\omega^2}$$

(2.13)

Let us consider the interaction term in Eqn (2.11) in more detail.

$$H_{int} = - \int D(r) \cdot P(r) \, d^3r = - \int D(r, r_{el}) \cdot P(r) \, d^3r$$

where $D(r)$ is written as $D(r, r_{el})$ for the field at r due to the electron at r_{el}. We further introduce the quantity $\phi(r)$ which is defined by the relation

$$4\pi \, \underset{\sim}{P}(\underline{x}) = \nabla_{\underline{x}} \, \phi(\underline{x})$$

(2.14)

so that $\phi(\underline{x})$ may be considered as the potential producing the polarization field $\underset{\sim}{P}(\underline{x})$. We may now write H_{int} using Eqns (2.9),(2.10) and (2.14) as

$$H_{int} = \frac{e}{4\pi} \int d^3x \left\{ \nabla_{\underline{x}} \left(\frac{1}{|\underline{x} - \underline{x}_{el}|} \right) \cdot \nabla_{\underline{x}} \, \phi(\underline{x}) \right\}$$

$$= e \, \phi(\underline{x}_{el})$$

(2.15)

where we have used the delta function property of (2.10) in solving for the integral.

The Hamiltonian now needs

$$H_{int} = \int d^3x \, \frac{\mu}{2} \left\{ \dot{P}^2(\underline{x}) + \omega^2 \, \underset{\sim}{P}^2(\underline{x}) \right\} + \frac{1}{2} m \, \dot{x}_{el}^2 + e \, \phi(\underline{x}_{el}) \; .$$

(2.16)

We now introduce the following variables $\underset{\sim}{B}(\underline{x})$ and $\underset{\sim}{B}^{\dagger}(\underline{x})$

$$\underset{\sim}{B}(\underline{x}) = \sqrt{\frac{\mu\omega^2}{2\hbar}} \left[\underset{\sim}{P}(\underline{x}) + \frac{i}{\omega} \, \dot{\underset{\sim}{P}}(\underline{x}) \right]$$

(2.17)

and

$$B^\dagger(\lambda) = \sqrt{\frac{\mu\omega}{2\hbar}} \left[P(\lambda) - \frac{i}{\omega} \dot{P}(\lambda) \right]$$

(2.18)

Since the conjugate variables $P(\lambda)$, $\mu \dot{P}(\lambda)$ satisfy the commutation relations

$$\left[P(\lambda), \mu \dot{P}(\lambda') \right] = i\hbar \, \delta(\lambda - \lambda')$$

(2.19)

the new variables $B(\lambda)$ and $B^\dagger(\lambda)$ can easily be shown to obey

$$\left[B(\lambda), B^\dagger(\lambda') \right] = \delta(\lambda - \lambda')$$

(2.20)

Expanding $B(\lambda)$ and $B^\dagger(\lambda)$ in terms of its Fourier components we may express

$$B(\lambda) = \frac{1}{\sqrt{V}} \sum_q \frac{q}{|q|} b_q \, e^{iq \cdot \lambda}$$

(2.21)

and

$$B^\dagger(\lambda) = \frac{1}{\sqrt{V}} \sum_q \frac{q}{|q|} b_q^\dagger \, e^{-iq \cdot \lambda}$$

(2.22)

where V is the volume of the media, and b_q, $b_q^\dagger$ may be shown (using Eqn (2.20)) to satisfy

$$[b_q, b_{q'}^\dagger] = \delta_{qq'} \; ; \; [b_q, b_{q'}] = [b_q^\dagger, b_{q'}^\dagger] = 0$$

(2.23)

The Hamiltonian (2.16) may now be expressed in terms of $b_q, b_q^\dagger$ after a lengthy but simple calculation in the following form

$$H = -\frac{\hbar^2}{2m} \nabla_{el}^2 + \sum_q \hbar\omega \left(b_q^\dagger b_q + \frac{1}{2}\right)$$

$$+ \frac{iU}{\sqrt{V}} \sum_q \frac{1}{|q|} \left[b_q^\dagger e^{-iq\cdot r} - b_q e^{iq\cdot r}\right]$$

(2.24)

where

$$U = \hbar\omega (4\pi\alpha)^{1/2} \left[\hbar/2m\omega\right]^{1/4}$$

(2.25)

and

$$\alpha = \frac{e^2}{\hbar} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right] \left(m/2\hbar\omega\right)^{1/2}$$

(2.26)

Since the operator b_q and $b_q^\dagger$ satisfy the commutation relations (2.23) it is possible to deduce that these operators acting on state

of the lattice described by $|n_q\rangle$ where n_q is the excitation number of the lattice mode q generate the following relations

$$b_q |n_q\rangle = \sqrt{n_q} \, |n_q - 1\rangle$$

(2.27)

and

$$b_q^\dagger |n_q\rangle = \sqrt{n_q + 1} \, |n_q + 1\rangle$$

(2.28).

It is customary to refer to $b_q^\dagger$ and b_q as creation and annihilation operators, respectively, for a lattice mode with wave vector q.

2 Free Polaron Energy

The Hamiltonian for an electron in a polar material as obtained in the previous section, reads

$$H = - \frac{\hbar^2}{2m} \nabla_{el}^2 + \sum_q \hbar\omega \left(b_q^\dagger b_q + \frac{1}{2} \right)$$

$$+ \frac{iU}{\sqrt{V}} \sum_q \frac{1}{|q|} \left[b_q^\dagger e^{-iq\cdot r} - b_q e^{iq\cdot r} \right]$$

$$(2.29)$$

where U is given by Eqn.(2.25) with Eqn.(2.26). The first term is the kinetic energy of an electron in a crystal with m as the effective mass. The second term is the energy of the lattice and the last term is the interaction between the electron and the lattice. Let the interaction be small so that it may be considered as perturbation to the unperturbed Hamiltonian given by the first two terms. The eigen state of the unperturbed Hamiltonian may be denoted by $|K, n_q\rangle$ where K is the wave vector of the electron and n_q is the excitation number of the qth lattice mode. The energy of the state $E_0(K, n_q) = \left(\hbar^2 K^2 / 2m \right) + \hbar\omega \left(n_q + \frac{1}{2} \right)$ If we restrict ourselves to temperatures very much below the Debye temperature the lattice vibrations may be assumed to have little or no excitation at all so that for all q's, $n_q = 0$. The unperturbed energy $E_0(K)$ corresponding to this state is $\hbar^2 K^2 / 2m$. We may now use the perturbation theory to calculate the change in the

energy $\Delta E(k)$ due to the interaction term. The change in the energy is expressed by

$$\Delta E = \langle k,0| H_{int} |k0\rangle + \sum_{k' n_q} \frac{|\langle k,0| H_{int} |k', n_q\rangle|^2}{E_0(k) - E_0(k', n_q)}$$

(2.30)

where $E_0(k, n_q) = \left(\hbar^2 k^2/2m\right) + \hbar\omega\left(n_q + \frac{1}{2}\right)$ and H_{int} is the interaction term given by

$$H_{int} = \frac{i U}{\sqrt{V}} \sum_q \frac{1}{|q|} \left[b_q e^{-i q \cdot r} - b_q e^{i q \cdot r} \right]$$

(2.31)

If we use the creation and annihilation properties of $b_q^{\dagger}$ and b_q it is easy to show that the first order perturbation term in (2.30) is zero and that second order connection can be rewritten as

$$\Delta E = \frac{U^2}{V} \sum_q \frac{1}{q^2} \frac{1}{\left(\hbar^2 k^2/2m\right) - \left(\hbar^2 (k-q)^2/2m\right) - \hbar\omega}$$

(2.32)

Changing summation over q to integration by

$$\sum_q \longrightarrow \frac{V}{8\pi^3} \int d^3 q \quad :$$

(2.33)

We obtain

$$\Delta E = \frac{U^2}{8\pi^3} \int_0^{2\pi} d\phi \int_0^{\infty} dq \int_{-1}^{+1} d\cos\alpha \left[\frac{1}{(-\hbar^2 q^2/2m) + (\hbar^2 Kq\cos\alpha/2m) - \hbar\ldots} \right.$$

$$(2.34)$$

We now consider electrons with small values of k so that the second term in the denominator is small and therefore develop the integrand in powers of k. It is then straightforward to perform integrations in Eqn (2.34) to give

$$\Delta E = -\frac{U^2 m}{2\hbar^2} \left[\left(\frac{\hbar}{2m\omega} \right)^{1/2} + \left(\frac{\hbar}{2m\omega} \right)^{3/2} \frac{k^2}{6} + \cdots \right]$$

$$(2.35)$$

Using the value of U from Eqn. (2.25) we may write the perturbed energy of an electron with wave vector $\underset{\sim}{k}$ according as

$$E(k) = \frac{\hbar^2 k^2}{2m} - \alpha\hbar\omega - \frac{\hbar^2 k^2}{2m} \frac{\alpha}{6}$$

$$(2.36)$$

If $\alpha = 0$, i.e., no perturbation, we obtain $E(k) = \frac{\hbar^2 k^2}{2m}$ as is expected. With the perturbation present the electron behaves like a free particle with energy

$$E(k) = \frac{\hbar^2 k^2}{2m^*} - \alpha\hbar\omega$$

$$(2.37)$$

where the mass of the electron with accompanying polarization field may to refered as polaron mass m^* which is related to the effective mass m by the relationship

$$m^* = \frac{m}{1 - (\alpha/6)}$$

(2.38).

It must be emphasized that Eqns.(2.35) to (2.38) are valid for small values of k only (i.e., for a slow electron). For electrons with a large value of k the energy cannot be described by the quadratic dependence on k . The polaron effects for slow electrons have received attention in literature while polaron effects for electrons with large k have been considered of no great significance.

We may interpret the result of electron lattice interaction on the motion of a slow electron to be equivalent to a free quasi particle motion with a renormalized mass m^* . The quasi particle is called a "polaron".

CHAPTER III

The Bound Polaron

In this chapter we calculate the ground state energy of a bound polaron in a polar media. In Section A we give the calculation of the problem first attempted by Platzman, while in Section B a new method of calculating ΔE is presented.

Section A

Platzman considered the following Hamiltonian for a system of an electron in a polar crystal and in the presence of a coulombic impurity atom.

$$H = -\frac{\hbar^2}{2m} \nabla^2_{r_{el}} + \vartheta + \sum_{q} \hbar\omega \left(b_q^\dagger b_q + \frac{1}{2} \right)$$

$$+ \frac{iU}{\sqrt{V}} \sum_{q} \frac{1}{q} \left(b_q^\dagger e^{-i\vec{q}\cdot\vec{r}} - b_q e^{i\vec{q}\cdot\vec{r}} \right)$$

$$(3.1)$$

The above Hamiltonian is similar to the Hamiltonian for a free polar, the difference being that in the case of a bound polaron the Hamiltonian has an added term ϑ corresponding to the potential energy of the electron in the presence of an impurity atom. If the interaction between the electron and the lattice is considered as

perturbation then the unperturbed Hamiltonian H_0 is

$$H_0 = -\frac{p^2}{2m} + V + \sum_{q} \hbar\omega \left(b_q^\dagger b_q + \frac{1}{2} \right)$$

(3.2)

The eigen state of the electron may be represented by $|n\rangle$ and that of the lattice by $|N_q\rangle$ for all values of q. The combined state may be expressed as $|N_q, n\rangle$. The energy corresponding to the state could then be written as $E^0(N_q, n)$. If the potential energy V is due to coulombic impurity then $|n\rangle$ will be hydrogen atom wave functions and

$$E^0(N_q, n) = -\frac{e^4}{2\epsilon^2 \hbar^2 n^2} + \sum_{q} \left(N_q + \frac{1}{2} \right) \hbar\omega$$

(3.3)

where ϵ is the dielectric constant of the media and n takes integral values. As before we shall restrict ourselves to temperatures well below the Debye temperatures so that $N_q \simeq 0$ for all q's and the eigen energies of interest therefore are

$$E^0(0, n) = \frac{-e^4}{2\epsilon^2 \hbar^2 n^2} + \sum_{q} \frac{\hbar\omega}{2} = E_n$$

(3.4)

The perturbed energy due to electron-lattice interaction may now be written, using the standard result of the second order perturbation theory, according to

$$E = E^0(o, n) + \Delta E$$

where

$$\Delta E = -\frac{U^2}{V} \sum_{q, n'} \frac{1}{q^2} \frac{\langle o, n| \, b_q^\dagger \, e^{-i q \cdot \lambda} + b_q \, e^{i q \cdot \lambda} |1_q \, n' \rangle \langle n' 1_q | \, b_q^\dagger \, e^{-i q \cdot \lambda} - b_q \, e^{i q \cdot \lambda} |0, n \rangle}{E^0(o, n) - E^0(1_q, n')}$$

$$= -\frac{U^2}{V} \sum_{q, n'} \frac{1}{q^2} \frac{\langle n| \, e^{i q \cdot \lambda} |n' \rangle \langle n' | \, e^{-i q \cdot \lambda} |n \rangle}{E_n - E_{n'} - \hbar \omega}$$

<div align="right">(3.5)</div>

In Eqn.(3.5) we have used a shorthand notation for $\langle o, n|$ as $\langle n|$. We are interested in calculating the change in energy ΔE due to perturbation of the ground state, so that in Eqn.(3.5) we substitute $n = 1$ so that state $|1\rangle$ is the ground state wave function of hydrogen atom and

$$\Delta E = \frac{U^2}{V} \sum_{q, n'} \frac{1}{q^2} \frac{\langle 1| \, e^{i q \cdot \lambda} |n' \rangle \langle n' | \, e^{-i q \cdot \lambda} |1 \rangle}{E_1 - E_{n'} - \hbar \omega}$$

<div align="right">(3.6).</div>

Exact evaluation of (3.6) is not possible. Approximate evaluation scheme as suggested by Platzman consists in using the following identity

$$-\frac{1}{E_1 - E_n - \hbar\omega} = \frac{1}{\hbar\omega + (\hbar^2 q^2/2m)} - \frac{E_n - E_1 - (\hbar^2 q^2/2m)}{(E_n - E_1 + \hbar\omega)(\hbar\omega + (\hbar^2 q^2/2m))}$$

(3.7)

By the method of iteration the above identity will generate a series solution for the left hand side according as

$$-\frac{1}{E_1 - E_n - \hbar\omega} = \frac{1}{\hbar\omega + (\hbar^2 q^2/2m)} + \frac{E_n - E_1 - (\hbar^2 q^2/2m)}{[\hbar\omega + (\hbar^2 q^2/2m)]^2} + \cdots$$

(3.8)

If we now substitute (3.7) into Eqn. (3.6) we may unite

$$\Delta E = \Delta E_1 + \Delta E_2.$$

(3.9)

where

$$\Delta E_1 = -\frac{U^2}{V} \sum_q \frac{1}{q^2} \sum_n \frac{\langle 1| e^{i\vec{q}\cdot\vec{r}_m}|n\rangle \langle n| e^{-i\vec{q}\cdot\vec{r}_m}|1\rangle}{\hbar\omega + (\hbar^2 q^2/2m)}$$

(3.10)

and

$$\Delta E_2 = \frac{U^2}{V} \sum_q \frac{1}{q^2} \sum_n \frac{[E_n - E_1 - (\hbar^2 q^2/2m)]\langle 1| e^{i\vec{q}\cdot\vec{r}_m}|n\rangle \langle n| e^{-i\vec{q}\cdot\vec{r}_m}|1\rangle}{(E_n - E_1 + \hbar\omega)[\hbar\omega + (\hbar^2 q^2/2m)]}$$

(3.11)

Since

$$\sum_n \langle 1 | e^{i\mathbf{q}'\cdot\mathbf{r}} | n \rangle \langle n | e^{-i\mathbf{q}\cdot\mathbf{r}} | 1 \rangle = 1$$

by the normalization condition, the integration over $\mathbf{q}$ in Eqn (3.10) may easily be performed to give

$$\Delta E_1 = -\frac{U^2}{4\pi} \sqrt{\frac{2m}{\omega \hbar^3}} = -\alpha \hbar\omega$$

(3.12)

In order to evaluate ΔE_2 we use the identity (3.7) and write

$$\Delta E_2 = \Delta E_3 + \Delta E_4$$

where

$$\Delta E_3 = \frac{U^2}{V} \sum_q \frac{1}{q^2} \sum_n \frac{\langle 1 | e^{i\mathbf{q}\cdot\mathbf{r}} [E_n - E_1 - (\hbar^2 q^2/2m)] n \rangle \langle n | e^{-i\mathbf{q}\cdot\mathbf{r}} | 1 \rangle}{[\hbar\omega + (\hbar^2 q^2/2m)]^2}$$

(3.13)

Remembering that $H_{el} | n \rangle = E_n | n \rangle$ and the property that

$$e^{i\frac{q \cdot \lambda}{\hbar}} H_{el}(\underset{\sim}{p}) e^{-i\frac{q \lambda}{\hbar}} = H_{el}(\underset{\sim}{p} - \hbar \underset{\sim}{q})$$

$$= H_{el}(\underset{\sim}{p}) + \frac{\hbar^2 q^2}{2m} - \frac{\hbar \underset{\sim}{p} \cdot \underset{\sim}{q}}{m}$$

(3.14)

where $H_{el} = \frac{p^2}{2m} + v$ (the electron Hamiltonian with p as momentum operator), we may rewrite

$$\Delta E_3 = \frac{U^2}{V} \sum_{q} \frac{\langle 1| \frac{\hbar}{m} \underset{\sim}{p} \cdot \underset{\sim}{q} |1\rangle}{q^2 [\hbar \omega + (\hbar^2 q^2 / 2m)]} = 0$$

(3.15)

The vanishing integral arises from the angular integration over the angle between $\underset{\sim}{p}$ and $\underset{\sim}{q}$. We may now calculate ΔE_4 which using our identity (3.7) can be broken up into two parts

$$\Delta E_4 = \Delta E_5 + \Delta E_6$$

where

$$\Delta E_5 = -\frac{U^2}{V} \sum_{\underset{\sim}{q}} \frac{1}{q^2} \sum_{n} \frac{[E_n - E_1 - (\hbar^2 q^2 / 2m)]^2 \langle 1| e^{i\frac{q \cdot \lambda}{\hbar}} |n\rangle \langle n| e^{-i\frac{q \cdot \lambda}{\hbar}} |1\rangle}{[\hbar \omega + (\hbar^2 q^2 / 2m)]^3}$$

(3.16).

Using the property (3.14) we are able to write

$$\Delta E_5 = -\frac{U^2}{V} \sum_{\underset{\sim}{q}} \frac{1}{q^2} \frac{\langle 1 | [H_{el} - E_1 - (\frac{\hbar}{\sim} \underset{\sim}{p} \cdot \underset{\sim}{q}/m)]^2 | 1 \rangle}{(\hbar\omega + (\hbar^2 q^2/2m))^3}$$

(3.17).

Evaluation of ΔE_5 is tedious but not difficult. Using hydrogen wave function for our state $| 1 \rangle$ it is possible to show that

$$\Delta E_5 = -\frac{1}{6} \alpha \beta^2 \hbar\omega$$

(3.18)

where

$$\beta^2 = -E_1 / \hbar\omega$$

(3.19)

If we put together terms $\Delta E_1, \Delta E_3$ and ΔE_5 we obtain

$$\Delta E = -\alpha \hbar\omega (1 + \frac{\beta^2}{6}) + \cdots$$

(3.20).

Platzman calculated higher terms in the expansion generated by Eqn (3.7) and obtained an expression ΔE valid up to the 4th power in β. His results were later corrected by Sak and also by Wang et al. These authors showed that ΔE up to the 4th power in β can be given by

$$\Delta E = - \alpha \hbar \omega \left(1 + \frac{\beta^2}{6} + \frac{\beta^4}{24} \right)$$

(3.21)

If the identity (3.7) is successively employed for calculating beyond Eqn. (3.21) then the expression for ΔE may be obtained consisting of higher powers in β. The use of the identity (3.7) generates a power series in β for the energy ΔE. The validity of Eqn (3.21) is therefore restricted to the condition that

$$\beta^2 << 1$$

(3.22).

Sak has also pointed out difficulties in calculating ΔE for higher power of β beyond the 4th power. In calculating higher order terms Sak showed that many of the integrals involved diverge. In the next section we have proposed a different approach for calculating ΔE. Unfortunately we have also encountered divergent integrals similar to those in the work of Sak.
We do not have a simple solution to avoid these difficulties and have not been able to propose a solution.

Section B

In this section we consider a new approach for calculating the change in the ground state energy of a bound electron due to electron-phonon interaction.

We start with the expression (3.6) from our last section and write

$$\Delta E = \frac{U^2}{V} \sum_{q, n'} \frac{\langle 1| e^{i q \cdot x} |n'\rangle \langle n'| e^{-i q \cdot x} |1\rangle}{q^2 (E_1 - E_n - \hbar\omega)}$$

$$(3.23).$$

We have seen, in the previous section, an expansion procedure adopted by Platzman to evaluate the quantity ΔE. In our procedure we employ the identity

$$-\int_0^\infty e^{(E_1 - E_n - \hbar\omega)t} \, dt = \frac{1}{E_1 - E_n - \hbar\omega}$$

$$(3.24)$$

where t is a variable of integration and has no obvious physical meaning. It should be noted that $E_1 - E_n - \hbar\omega$ is negative since E_1 is the ground state energy and $E_1 \leq E_n$. Employing the identity (3.24) it is possible to express (3.23) in the following form

$$\Delta E = -\frac{U^2}{(2\pi)^3} \sum_n \int dq \int_0^\infty dt \, e^{(E_1 - \hbar\omega)t} \langle 1| e^{i q \cdot x} e^{-E_n t} |n'\rangle$$
$$\times \langle n'| e^{-i q \cdot x} |1\rangle$$

$$(3.25)$$

where we have changed summation over q to integration using (2.33).

The following relations

$$H_{el}(\underline{p}) \, | n' \rangle = E_{n'} \, | n' \rangle$$

<div align="right">(3.26)</div>

and the property (3.14)

$$e^{i\underline{q}\cdot\underline{x}} \, H_{el}(\underline{p}) \, e^{-i\underline{q}\cdot\underline{x}} = H_{el}(\underline{p}-\hbar\underline{q})$$

$$= H_{el} + \frac{\hbar^2 q^2}{2m} - \frac{\hbar \, \underline{p}\cdot\underline{q}}{m}$$

<div align="right">(3.27)</div>

enable us to rewrite Eqn (3.25) according to

$$\Delta E = -\frac{U^2}{8\pi^3} \int_0^\infty dt \int dq \; e^{-(E_1-\hbar\omega)t} \langle 1 | \, e^{-H_{el}(\underline{p}-\hbar\underline{q})} \, | 1 \rangle$$

<div align="right">(3.28).</div>

For the sake of convenience of shorthand notation we define

$$H_{el}(\underline{p}-\hbar\underline{q}) = -\frac{\hbar^2 q^2}{2m} + A + V$$

<div align="right">(3.29)</div>

where

$$A = -\frac{\hbar^2 p^2}{2m} + \frac{\hbar\, p\cdot q}{m} \quad ; \quad V = \frac{-e^2}{\epsilon\, r}$$

(3.30)

so that

$$\Delta E = -\frac{U^2}{8\pi^3}\int dq \int dt\; e^{[E_1 - \hbar\omega - (\hbar^2 q^2/2m)]t}$$

$$\times \langle 1| e^{(A-V)t} |1\rangle$$

(3.31)

The expression for ΔE given by Eqn (3.31) is exact. We now employ approximation scheme by writing

$$e^{(A-V)t} = e^{At} - Vt + (V^2 - AV - VA)(t^2/2)$$

$$+ (AVA + A^2V + VA^2 \cdots)(t^3/6)$$

(3.32)

where it should be noted that the operator A does not commute with V.

Substituting expansion (3.32) into Eqn (3.31) we may write

$$\Delta E = \Delta E' + \Delta E'' + \Delta E''' + \Delta E^{iv}$$

(3.33)

where

$$\Delta E^{'} = -\frac{U^2}{8\pi^3} \int dq \int_0^\infty dt \, e^{[E_1 - \hbar w - (\hbar^2 q^2/2m)]t} \langle 1| \, e^{At} \, |1\rangle$$

(3.34)

$$\Delta E^{''} = \frac{U^2}{8\pi^3} \int dq \int_0^\infty dt \, e^{[E_1 - \hbar w - (\hbar^2 q^2/2m)]t} \langle 1| \, vt \, |1\rangle$$

(3.35)

$$\Delta E^{'''} = \frac{U^2}{8\pi^3} \int dq \int_0^\infty dt \, e^{[E_1 - \hbar w - (\hbar^2 q^2/2m)]t}$$
$$\times \langle 1| \, Av + vA - v^2 \, |1\rangle$$

(3.36)

and

$$E^{iv} = -\frac{U^2}{8\pi^3} \int dq \int_0^\infty dt \, e^{[E_1 - \hbar w - (\hbar^2 q^2/2m)]t}$$
$$\times \langle 1| \, AvA + A^2v + vA^2 + \cdots |1\rangle$$

(3.37)

We have restricted ourselves to the four terms arising from
Eqn (3.32).

Physically the expression $\Delta E'$ is obtained by neglecting the potential energy from E_n. For states $E_n < 0$ the potential energy is larger then the kinetic energy and the approximation would be unrealistic. For $E_n > 0$ (i.e., unbound states), however, the kinetic energy is greater than the potential energy and for these states the approximation would be at least reasonable. The approximation would still be reasonable if the contribution to $\Delta E'$ due to all unbound states is significantly larger than due to bound state. For a strongly bound electron a larger number of unbound state would be coupled with the ground state than in the case of weakly bound electron. Our result for $\Delta E'$ is therefore more adequate for the case of strongly bound ground state. The terms $\Delta E''$ to ΔE^{iv} take into account the effect of the potential which is completely neglected in $\Delta E'$.

The integral in Eqns. (3.34) to (3.36) can be evaluated by lengthy but straightforward calculations. The integral (3.37) is however quite complicated and we have evaluated this integral only up to terms whose contribution is comparable to the integral in (3.36). The result of integration gives

$$\Delta E' = -\left(\frac{8}{3}\right) \alpha \, \hbar \omega \left(1 + \beta^2\right)^{1/2} \left\{ \frac{3}{8} - \frac{\beta^2}{2} + \beta^4 \left[1 - \left(\beta^2 / 1 + \beta^2\right)^{1/2} \right] \right\}$$

$$(3.38)$$

$$\Delta E'' = -\alpha \hbar \omega \; \beta^2 (1+\beta^2)^{-3/2}$$

$$(3.39)$$

$$\Delta E''' = (3/2) \alpha \hbar \omega \; \beta^4 (1+\beta^2)^{-5/2}$$

and $$(3.40)$$

$$\Delta E^{IV} = (-7/6) \alpha \hbar \omega \; \beta^4 (1+\beta^2)^{-5/2}$$

so that $$(3.41)$$

$$\Delta E = \alpha \hbar \omega \left\{ -\frac{8}{3} (1+\beta^2)^{1/2} \left[\frac{3}{8} - \frac{\beta^2}{2} + \beta^4 \left(1 + (\beta^2/{1+\beta^2})^{1/2}\right) \right] \right. $$
$$\left. - \beta^2 (1+\beta^2)^{-3/2} + (1/3) \beta^4 (1+\beta^2)^{-5/2} \right\}$$

$$(3.42).$$

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Discussion:

We may now compare our expression (3.42) for ΔE with the corresponding expression (3.21) given by Platzman. If we consider the case when $\beta \ll 1$ and expand our expression (3.42) in power of β and retain up to the 4th power in β then our expression reduces exactly to the result of Platzman (Eqn. (3.21)). In the limit of $\beta \rightarrow \infty$ our expression for ΔE goes to zero. The electron-phonon interaction has therefore no effect on the grand state energy of electron. In this case one may conclude that the phonon cloud is enable to follow the electron motion and therefore the polaron effects are negligible. A graph showing the dependence of ΔE on β for Plazman's and our results is given in Fig. 1.

One may conclude that Platzman's result is valid for only small values of β while our expression takes into account small and large values for β within the limitations indicated.

Acknwoledgement

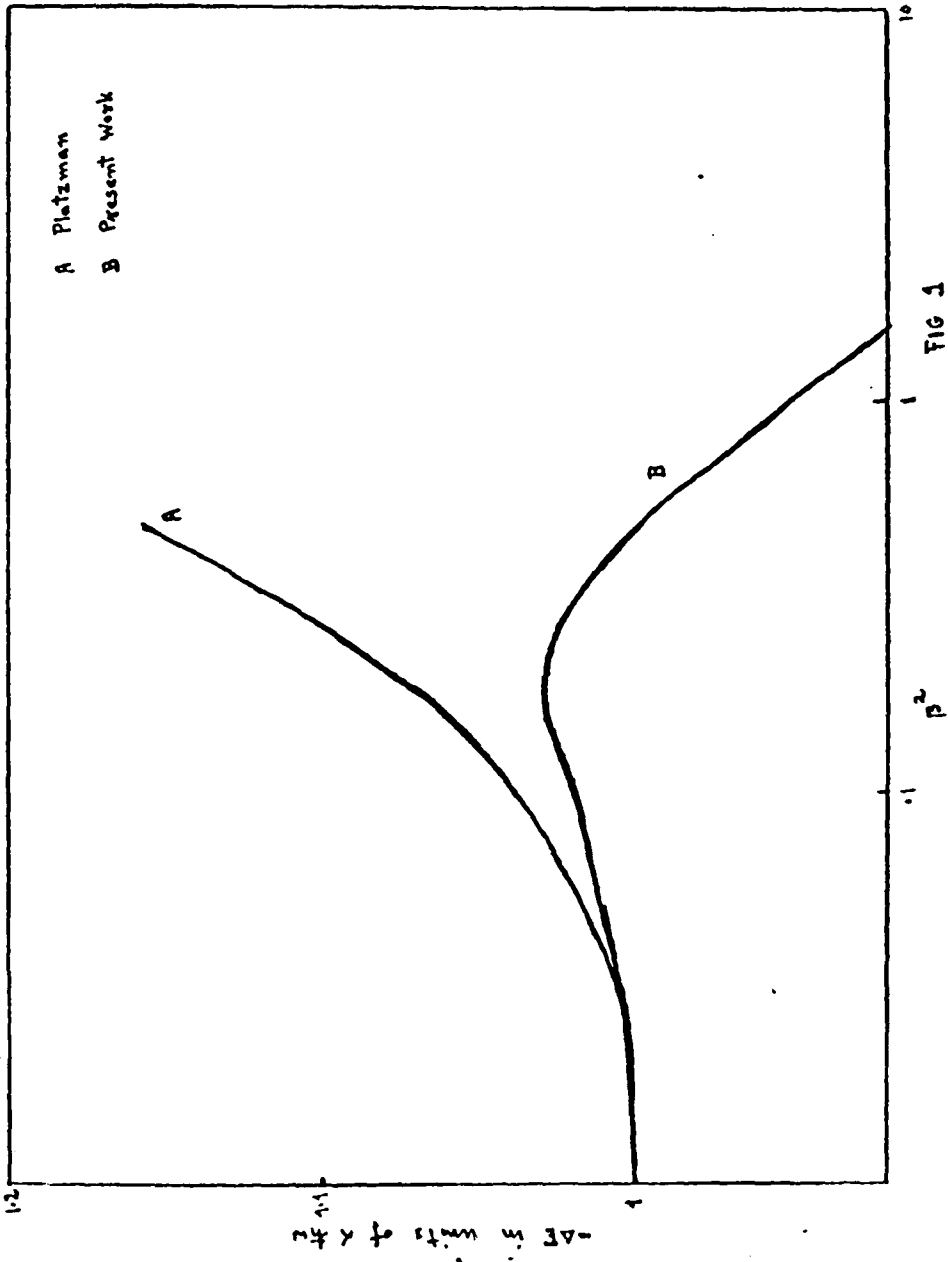FIG 1

A Platzman
B Present work

$-\Delta E$ in units of $k^2 f_w$

REFERENCES

Fröhlich, H., Advances in Physics 3, 325, (1954).

Pelkar, S., J. of Physics (U.S.S.R.) 10, 341, (1946).

Platzman, P. M., Phys. Rev. 125, 1061, (1962).

Sak, J., Phys. Rev. 13, 3, 3356, (1971).

Wang, S., Arora, H. L., Matsuura, M., Phys. Rev. B4, 3685 (1971).

POLARON BOUND TO A COULOMB POTENTIAL

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The problem of an electron bound to a coulomb impurity center embedded in an ionic semiconductor and interacting with optical phonons has been of considerable interest in recent years.[1-4] Platzman[1] was the first to calculate the ground state energy, E, of an electron for such a system. He considered the electron-phonon interaction as perturbation and used the second order perturbation theory to obtain the result. The validity of his calculations is, however, restricted to situations where the ratio $\beta^2 = E_1/\hbar\omega$ of the unperturbed ground state energy, E_1, to the energy, $\hbar\omega$, of an optical phonon is very much smaller than unity. The expression for E according to Platzman and including the recent extensions proposed by Sak[2] can be written as

$$E = E_1 - \alpha\hbar\omega\left[1 + (\beta^2/6) + (\beta^4/24)\right], \text{ provided } \beta^2 \ll 1; \quad (1)$$

where

$$\alpha = \frac{e^2}{\hbar}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\left(m/2\hbar\omega\right)^{1/2} \quad (2)$$

In Eqn. (2), e is the electronic charge, m the effective band electron mass, ϵ_∞ and ϵ_0 are respectively the high and low frequency dielectric constants of the material. Sak[2] has shown that the result, as expressed by Eqn. (1), cannot be extended to include higher powers of β by using Platzman's procedure.

Bajaj[3] following the work of Delgarno and Lewis[5] attempted the problem by using a method different from that used by Platzman and

obtained the expression for E valid for the complete range of values for β. A result similar to that of Bajaj was also obtained by Stoneham.[4] The conclusions arrived at by these two authors were criticized by Larsen[5] who showed that the expression for E obtained by them does not reduce to the result of Platzman, as given by Eqn. (1), in the limit of small β and that their result may hold only in the limit of an extremely weak electron binding situation.

It is the purpose of this communication to propose a method for calculating E for values of β within and beyond the range prescribed in Eqn. (1), and to show that our expression for E agrees exactly with the result of Platzman - (Eqn. (1)) - in the limit of small β, while for large β the expression for E reduces to a result which is expected on physical considerations.

The Hamiltonian, H, of our system may be expressed in terms of usual notation by

$$H = (p^2/2m) - (e^2/\epsilon_\infty r) + \sum_q \hbar \omega \, a_q^* a_q$$

$$+ \frac{iU}{(v)^{1/2}} \sum_q [a_q^* \exp(-iq \cdot r) - a_q \exp(iq \cdot r)] , \tag{3}$$

where

$$U = \hbar \omega \, (4\pi\alpha)^{1/2} (\hbar/2m\omega)^{1/4} \tag{4}$$

and a_q^*, a_q are the usual creation / destruction operators for a lattice mode of wave vector q.

Treating the electron-phonon interaction as perturbation we can write the energy E of the ground state $|1\rangle$ at zero temperature

by using the second order perturbation theory accordingly as

$$E = E_1 + \frac{U^2}{(2\pi)^3} \sum_n \int dq \frac{\langle 1| \exp(i q \cdot x)|n\rangle \langle n| \exp(-i q \cdot x)|1\rangle}{q^2 (E_1 - E_n - \hbar\omega)} \quad , \quad (5)$$

where $|n\rangle$ is the unperturbed eigen state corresponding to energy E_n given by

$$\left[(p^2/2m) + (e^2/\epsilon_c x) \right] |n\rangle = E_n |n\rangle \quad . \quad (6)$$

In order to evaluate E in Eqn. (5), we use the following identity

$$\frac{1}{E_1 - E_n - \hbar\omega} = - \int_0^\infty \exp\left[(E_1 - E_n - \hbar\omega)t\right] dt \quad , \quad (7)$$

so that Eqn. (5) can easily be shown to be

$$E = E_1 - \frac{U^2}{(2\pi)^3} \int dt \int \frac{dq}{q^2} \exp\left[(E_1 - \hbar\omega)t\right]$$

$$\times \langle 1| \exp\left[-H(p - \hbar q)t\right]|1\rangle \quad , \quad (8)$$

using the relation[1]

$$\exp(i q \cdot x) H(p) \exp(-i q \cdot x) = H(p - \hbar q) \quad (9)$$

where

$$(10)$$

$$H(p - \hbar q) = \frac{(p - \hbar q)^2}{2m} - \frac{e^2}{\epsilon_0 x}$$

We now employ a shorthand notation A for the operator $\left[-(p^2/2m) + (\hbar\, p \cdot q/m)\right]$ and V for $(-e^2/\epsilon_o \lambda)$ and re-write Eqn. (8) in terms of A and V as

$$E = E_1 - \frac{U^2}{(2\pi)^3} \int \frac{d \cdot q}{q^2}\, exp\left\{[E_1 - \hbar\omega - (\hbar^2 q^2/2m)]t\right\}$$

$$\times \langle 1| exp[(A-V)t] |1\rangle . \tag{11}$$

Expanding the operator $exp[(A-V)t]$ in powers of t for V up to third power in t, we write

$$exp[(A-V)t] = exp(At) - Vt + (V^2 - AV - VA)(t^2/2)$$

$$- (AVA + A^2V + VA^2 + \cdots)(t^3/6) . \tag{12}$$

We now use Eqn. (12) in Eqn. (11) and write

$$E = E_1 + E' + E'' + E''' + E^{iv} \tag{13}$$

where

$$E' = -\frac{U^2}{(2\pi)^3} \int \frac{dq}{q^2} \int_0^\infty dt\, exp\left\{[E_1 - \hbar\omega - (\hbar^2 q^2/2m)]t\right\}$$

$$\tag{14}$$

$$\times \langle 1| exp(At) |1\rangle$$

$$E'' = \frac{U^2}{(2\pi)^3} \int \frac{dq}{q^2} \int_0^\infty dt \; \exp\left\{ [E_1 - \hbar\omega - (\hbar^2 q^2/2m)]t \right\}$$

$$\times \langle 1| \; Vt \; |1\rangle \; , \tag{15}$$

$$E''' = \frac{U^2}{(2\pi)^3} \int \frac{dq}{q^2} \int_0^\infty dt \; \exp\left\{ [E_1 - \hbar\omega - (\hbar^2 q^2/2m)]t \right\}$$

$$\times \langle 1| \; AV + VA - V^2 |1\rangle \; , \tag{16}$$

and

$$E^{iv} = \frac{U^2}{(2\pi)^3} \int \frac{dq}{q^2} \int_0^\infty dt \; \exp\left\{ [E_1 - \hbar\omega - (\hbar^2 q^2/2m)]t \right\}$$

$$\times \langle 1| \; AVA + A^2 V + VA^2 + \cdots \cdots |1\rangle \; . \tag{17}$$

Integrals in Eqns. (14), (15) and (16) can be evaluated exactly by lengthy but straightforward calculations. The integral in Eqn. (17) is, however, quite complicated. We are able to calculate this integral only up to terms whose contribution to E is comparable to the contribution by the integral in Eqn. (16). The Eqns. (14)-(17) after integration give

$$E' = -\frac{8}{3} \alpha \hbar \omega (1 + \beta^2)^{1/2} \left\{ \frac{3}{8} - \frac{\beta^2}{2} + \beta^4 \left[1 - (\beta^2/1 + \beta^2)^{1/2} \right] \right\} \tag{18}$$

$$E'' = -\alpha \hbar \omega \beta^2 (1 + \beta^2)^{-(3/2)} \tag{19}$$

$$E''' = (3/2) \alpha \hbar \omega \beta^4 (1 + \beta^2)^{-(5/2)} \tag{20}$$

and

$$E^{iv} = (-7/6) \alpha \hbar \omega \beta^4 (1 + \beta^2)^{-(5/2)} \tag{21}$$

so that

$$E = E_o + \alpha \hbar \omega \left\{ -\frac{8}{3} (1 + \beta^2)^{1/2} \left[\frac{3}{8} - \frac{\beta^2}{2} + \beta^4 \left\{ 1 - (\beta^2/1 + \beta^2)^{1/2} \right\} \right] - \beta^2 (1 + \beta^2)^{-3/2} + (1/3) \beta^4 (1 + \beta^2)^{-5/2} \right\} \tag{22}$$

The expression for E as given by Eqn. (22) represents the main conclusion of our communication.

We may now wish to compare our expression for E with the expressions obtained by other authors. First we compare our result with that of Platzman[1] and Sak[2] as given by Eqn. (1). Assuming $\beta^2 << 1$ we expand the right hand side of Eqn. (22) and considering terms up to the fourth power in β we observe that our expression for E reduces to Eqn. (1) exactly. On the other hand if we consider β to be large so that in the limit of β tending to infinity our expression becomes limit $\beta \rightarrow \infty$ $E = E_1$. This result is expected as it shows that in this limit phonon cloud is unable to follow the electron motion so that the electron phonon interaction has no effect on E. Of course, this does not mean that the ionization energy is unaffected by the interaction, since the energy corresponding to the bottom of the conduction band shifts by $\propto \hbar\omega$.

The proposed method for calculating E cannot be extended by considering higher terms in the expansion (12) since the integrals involved would be divergent, similar to those found by Sak.[2] This may, therefore, mean that our result for E would give excellent values for the weak electron binding case, but for a strong binding situation our result may only provide a reasonable estimate.

R E F E R E N C E S

[1] Platzman, P.M., *Phys. Rev.*, 125, 1061, 1962.

[2] Sak, J., *Phys. Rev.*, B, 3, 3356, 1971.

[3] Bajaj, K.K., *Solid State Communications*, 8, 1665, 1970.

[4] Stoneham, A.M., *J. Phys.*, C, 3, L134, 1970.

[5] Dalgarno, A. and Lewis., J.T., *Proc. Roy. Soc.*, 70, 1955.

[6] Larsen, D.M., *J. Phys.*, C, 3, L186, 1970.