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A REVIEW OF LARGE POLARONS
IN THE LOW TEMPERATURE LIMIT
AND OF SMALL POLARONS
IN THE HIGH TEMPERATURE LIMIT

OCTOBER 1968

AEC RESEARCH &
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UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

A REVIEW OF LARGE POLARONS IN THE LOW
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by

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FIRST UNDESTRUCTED
DUPLICATION

NOV 11 1968

October 1968

BATTELLE MEMORIAL INSTITUTE
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ABSTRACT

A comprehensive review is given of the theory of large polarons in the low temperature limit and of small polarons in the high temperature limit. Where possible reference is made to the applicability of small polaron theory to electrical conduction in some metal oxide insulators. The purpose of the report is to give the theoretical foundations and approximations inherent in small polaron theory in order to facilitate applications of the theory toward explaining electrical conduction in some metal oxide insulators.

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INTRODUCTION

This report was motivated by the suggestion that polaron conduction might be an important mechanism in certain insulators at high temperatures. Although polaron theory has been of interest at least since 1950⁽¹⁾ it was not until recently that the polaron concept received unambiguous experimental justification in a substance⁽²⁾ (TiO_2). There is reason to suspect that behavior characteristic of polarons is exhibited in other substances as well.⁽³⁻⁵⁾

A polaron consists of an extra electron in an insulator plus the phonon cloud about the electron arising from the lattice polarization induced by the electron. In the limit of low temperatures and weak electron-lattice coupling, the polaron is not well localized and is called a "large" polaron. The theory of large polarons in this limit is not distinct from band theory. In the limit of high temperatures and strong electron-lattice coupling, the polaron is well localized and is called "small" polaron theory. Although the theory of small polarons is what we are specifically interested in, we will gain perspective by also discussing the theory of large polarons.

The spirit of this report is that of a review. It was felt that a background study of polaron theory would be of use to further investigators. Some care was taken to keep the formalism self-contained and complete. As

the recipient of a Richland Faculty Appointment of three-month duration, I felt that the scope of this study closely matched the available time.

THEORY OF LARGE POLARONS

The material of this section closely follows the weak coupling theory of Fröhlich⁽⁶⁾ and the intermediate coupling theory of Lee, Low, and Pines.⁽⁷⁻⁸⁾ Steps missing in the formalism as it appears in the literature are generally entered here explicitly.

Strong coupling theory⁽⁹⁾ is not treated here except in the high temperature limit where small polaron theory is appropriate.

Building a Classical Hamiltonian

The classical Hamiltonian will be obtained in a two-step process. First, the lattice is treated without an extra electron and the contribution to the energy is calculated. Second, an extra electron is placed in the lattice and the modification of the Hamiltonian is derived. The reader will notice the macroscopic nature of the derivation. This is quite appropriate in the weak and intermediate coupling regions since the polaron is large compared to a single lattice spacing and is not very sensitive to the detailed structure of the lattice.

Consider, then, the lattice without the extra electron. In the absence of an external source of polarization, the lattice polarization arises purely from lattice vibration. For simplicity we assume no dispersion so that

$$\ddot{\vec{P}}(\vec{r}) + \omega^2 \vec{P}(\vec{r}) = 0 \quad , \quad (1)$$

where $\vec{P}(\vec{r})$ is the polarization at $\vec{r}$ and ω is the natural lattice frequency.

Since this is the harmonic oscillator equation, multiply throughout by $\dot{\vec{P}}(\vec{r})$ to obtain something proportional to the time rate of change of the energy density. Calling the proportionality constant μ , we have

$$\left(\frac{\text{energy}}{\text{density}}\right) = \frac{\mu}{2} \left(\dot{\vec{P}}^2(\vec{r}) + \omega^2 \vec{P}^2(\vec{r}) \right) \quad (2)$$

In Appendix A, μ is shown to be given by the equation

$$\mu = \frac{4\pi\bar{\epsilon}}{\omega^2}, \quad (3)$$

$\bar{\epsilon}$ being the average dielectric constant defined in Equation (A10).

If we now allow the extra electron into the lattice it will furnish a field $\vec{D}(\vec{r})$ to interact with the lattice polarization $\vec{P}(\vec{r})$. The interaction energy density between an externally applied field $\vec{D}(\vec{r})$ and a polarization (dipole) field $\vec{P}(\vec{r})$ is just $-\vec{D}(\vec{r}) \cdot \vec{P}(\vec{r})$. To this point we have accrued a total energy density

$$\frac{\mu}{2} \left(\dot{\vec{P}}^2(\vec{r}) + \omega^2 \vec{P}^2(\vec{r}) \right) - \vec{D}(\vec{r}) \cdot \vec{P}(\vec{r}) \quad (4)$$

Noting that the second and third terms are potential energy densities we change their signs to write a Lagrangian energy density

$$L' = \frac{\mu}{2} \left(\dot{\vec{P}}^2(\vec{r}) - \omega^2 \vec{P}^2(\vec{r}) \right) + \vec{D}(\vec{r}) \cdot \vec{P}(\vec{r}) \quad (5)$$

Continuing to build the classical Hamiltonian in the usual way, generalized coordinates are defined by

$$\vec{q}_r = \vec{P}(\vec{r}) \quad (6)$$

so that the conjugate momenta are given by

$$\vec{p}_r = \frac{\partial}{\partial \dot{\vec{q}}_r} L' = \mu \dot{\vec{P}}(\vec{r}) \quad (7)$$

Thus, the Lagrangian energy density becomes

$$L' = \frac{\vec{p}_r^2}{2\mu} - \frac{\mu\omega^2}{2} \vec{q}_r^2 + \vec{D}(\vec{r}) \cdot \vec{q}_r \quad (8)$$

with a corresponding Lagrangian

$$L' = \int d^3r L' \quad (9)$$

The Hamiltonian defined in terms of L' is

$$H' = \int d^3r \vec{q}_r \cdot \vec{p}_r - L' \quad (10)$$

Define a Hamiltonian energy density as the integrand of Equation (10); i.e.,

$$H' = \frac{\vec{p}_r^2}{2\mu} + \frac{\mu\omega^2}{2} \vec{q}_r^2 - \vec{D}(\vec{r}) \cdot \vec{q}_r \quad (11)$$

The equation of motion that is interesting is

$$\vec{p}_r = - \frac{\partial H'}{\partial \vec{q}_r} = -\mu\omega^2 \vec{q}_r + \vec{D}(\vec{r}) \quad (12)$$

In terms of the polarization Equation (12) becomes

$$\vec{p}(\vec{r}) + \omega^2 \vec{p}(\vec{r}) = \frac{1}{\mu} \vec{D}(\vec{r}) \quad (13)$$

Comparison to Equation (1) shows that introduction of the extra electron involves the term $\vec{D}(\vec{r})/\mu$. Equation (13) is used in Appendix A to evaluate μ .

What terms have not yet appeared in the Hamiltonian? The lattice energy and the electron-lattice vibration interaction have appeared but we have not yet added in the electron kinetic energy nor the interaction of the electron with the rigid lattice. In fact, we shall combine these two missing terms in the electron kinetic energy term by defining an effective mass m . Hence, the total Hamiltonian becomes

$$H = \vec{p}_{el}^2/2m + H' \quad (14)$$

where $\vec{p}_{el}$ is the electron momentum and m is an effective mass which includes the effect of the interaction of the electron with the rigid lattice. Later

we shall define a polaron effective mass and relate it to this electron effective mass.

Our final modification of the Hamiltonian follows from the realization that the important mode of polarization will be a longitudinal mode.⁽¹⁰⁾ A qualitative argument can be constructed by considering that the volume polarization charge density is given by $(\vec{\nabla} \cdot \vec{P})$. Now $(\vec{\nabla} \cdot \vec{P})$ vanishes for transverse modes but not for longitudinal modes. Since a non-zero charge density occurs only for the longitudinal $\vec{P}$ we expect the long-range interaction between the electron and this charge density will dominate any short range contributions from the interaction of the electron with a transverse $\vec{P}$.

Assuming, then, that $\vec{P}$ is longitudinal we note at once that

$$\vec{\nabla} \times \vec{P}(\vec{r}) = 0 \quad (15)$$

suggesting that we write

$$4\pi P(\vec{r}) = \vec{\nabla} \phi(\vec{r}) \quad (16)$$

Equation (16) allows that part of the Hamiltonian governing the electron-lattice polarization interaction to be simplified. Call that piece of the Hamiltonian H_{int} so

$$\begin{aligned} H_{int} &= -\int d^3r \vec{D} \cdot \vec{P} = -\int d^3r \vec{D} \cdot \vec{\nabla} \phi / 4\pi \\ &= -\frac{1}{4\pi} \int d^3r \left[\vec{\nabla} \cdot (\phi \vec{D}) - \phi \vec{\nabla} \cdot \vec{D} \right] \end{aligned} \quad (17)$$

Now the term with integrand $\left[\vec{\nabla} \cdot (\phi \vec{D}) \right]$ can be converted to a surface integral which will vanish if we demand that the electron is in the interior of a very large crystal. Hence, Equation (17) becomes

$$\begin{aligned} H_{int} &= \frac{1}{4\pi} \int d^3r \phi \vec{\nabla} \cdot \vec{D} \\ &= \frac{1}{4\pi} \int d^3r \phi(\vec{r}) 4\pi e \delta(\vec{r} - \vec{r}_{el}) \\ &= e \phi(\vec{r}_{el}) \end{aligned} \quad (18)$$

where $\vec{r}_{e1}$ is the position of the electron.

In summary, the classical Hamiltonian is written as the sum of three parts

$$H = H_{e1} + H_{ph} + H_{int} \quad , \quad (19)$$

where

$$H_{e1} = \vec{p}_{e1}^2 / 2m \quad , \quad (20)$$

$$H_{ph} = \frac{\mu}{2} \int d^3r \left[\vec{p}^2(\vec{r}) + \omega^2 \vec{p}^2(\vec{r}) \right] \quad (21)$$

and H_{int} is given by Equation (18).

Building a Quantal Hamiltonian

It is convenient to apply periodic boundary conditions. Consider a cubic region of side L and, hence, volume

$$V = L^3 \quad (22)$$

where V is large compared to any volume of interest. The crystal consists of many such cubic volumes each with its extra electron. Since there are now lots of electrons instead of just one, there will be a Coulomb interaction among all the extra electrons. For an infinite crystal this Coulomb energy diverges; however, we shall later indicate how this formal difficulty can be circumvented.

We expand the polarization vector in the sum

$$\vec{p}(\vec{r}, t) = \sum_{\vec{k}} \vec{p}_{\vec{k}}(t) e^{i\vec{k} \cdot \vec{r}} \quad , \quad (23)$$

where the periodicity of the lattice requires

$$k_i = \frac{2\pi}{L} n_i \quad , \quad n_i = 0, 1, 2, \dots \quad (24)$$

The quantal Hamiltonian is to be constructed from the classical Hamiltonian by applying the quantization condition on the coordinates and conjugate momenta,

$$[P_j(\vec{r}) , P_i(\vec{r}')] = i\hbar \delta_{ji} \delta(\vec{r} - \vec{r}') . \quad (25)$$

Now since we demand that $\vec{P}$ and $\dot{\vec{P}}$ be real, application of this condition to Equation (23) will partially destroy the independence of the coefficients $\vec{P}_{\vec{k}}$. Thus, the coefficients $\vec{P}_{\vec{k}}$ will not be a convenient choice of generalized coordinates for the Hamiltonian and we introduce, in place of $\vec{P}(\vec{r})$, a complex field $\vec{B}(\vec{r})$ whose Fourier coefficients are independent.

We define the complex field $\vec{B}(\vec{r})$ by

$$\vec{B}(\vec{r}) = \sqrt{\frac{\mu\omega}{2\hbar}} \left[\vec{P}(\vec{r}) + \frac{i}{\omega} \dot{\vec{P}}(\vec{r}) \right] . \quad (26)$$

Now the longitudinal nature of $\vec{P}$ demands that $\vec{P}_{\vec{k}}$ be in the $\vec{k}$ direction so when we Fourier analyze $\vec{B}$ we obtain

$$\vec{B}(\vec{r},t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \hat{k} b_{\vec{k}}(t) e^{i\vec{k}\cdot\vec{r}} . \quad (27)$$

Application of the quantization condition of Equation (25) to Equation (26) yields

$$[B_j(\vec{r}) , B_i^*(\vec{r}')] = \delta_{ji} \delta(\vec{r} - \vec{r}') . \quad (28)$$

Combining Equations (27) and (28) gives a quantization condition for the Fourier coefficients $b_{\vec{k}}$,

$$[b_{\vec{k}} , b_{\vec{k}'}^*] = \delta_{\vec{k},\vec{k}'} . \quad (29)$$

It is also obvious that

$$[b_{\vec{k}} , b_{\vec{k}'}] = 0 = [b_{\vec{k}}^* , b_{\vec{k}'}^*] \quad (30)$$

From Equations (29) and (30) it is clear that $b_{\vec{k}}^*$ and $b_{\vec{k}}$ may be interpreted respectively as phonon creation and annihilation operators. The product $b_{\vec{k}}^* b_{\vec{k}}$ is the phonon number operator.

Now we wish to take H_{ph} defined by Equation (21) and express it in terms of the creation and annihilation operators introduced above. To do so Equation (26) must be inverted and gives

$$\begin{aligned}\vec{P}(\vec{r}) &= \sqrt{\hbar/2\mu\omega} \left(\vec{B}^*(\vec{r}) + \vec{B}(\vec{r}) \right) , \\ \vec{P}(\vec{r}) &= \sqrt{\hbar\omega/2\mu} \left(\vec{B}^*(\vec{r}) - \vec{B}(\vec{r}) \right) .\end{aligned}\quad (31)$$

Equation (30) is then substituted into Equation (21); $\vec{B}(\vec{r})$ and $\vec{B}^*(\vec{r})$ are replaced via Equation (27) and the result is

$$H_{ph} = \sum_{\vec{k}} \hbar \omega (b_{\vec{k}}^* b_{\vec{k}} + \frac{1}{2}) . \quad (32)$$

It is customary to remove the zero point energy $\frac{\hbar\omega}{2}$ by redefining the energy origin. In that case, Equation (32) becomes

$$H_{ph} = \sum_{\vec{k}} \hbar \omega b_{\vec{k}}^* b_{\vec{k}} . \quad (33)$$

The next step in the building of the quantal Hamiltonian is to rewrite H_{int} as defined in Equation (18). The task is to rewrite the polarization potential ϕ of Equation (16) in terms of the phonon operators. From the first of Equation (31) and from Equation (27) we have

$$\vec{P}(\vec{r}) = \sqrt{\hbar/2\mu\omega V} \sum_{\vec{k}} \hat{k} \left(b_{\vec{k}}^* e^{-i\vec{k}\cdot\vec{r}} + b_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \right) . \quad (34)$$

By inspection of Equations (34) and (16) it follows immediately that

$$\phi(\vec{r}) = 4\pi i \sqrt{\frac{\hbar}{2\mu\omega V}} \sum_{\vec{k}} \frac{1}{k} \left(b_{\vec{k}}^* e^{-i\vec{k}\cdot\vec{r}} - b_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \right) . \quad (35)$$

Combining this last equation with Equation (18) yields

$$H_{\text{int}} = \sum_{\vec{k}} \left(v_{\vec{k}} b_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} + v_{\vec{k}}^* b_{\vec{k}}^* e^{-i\vec{k} \cdot \vec{r}} \right) , \quad (36)$$

where

$$v_{\vec{k}} = - \frac{i\hbar\omega}{k} \left[\hbar/2m\omega \right]^{1/4} \sqrt{4\pi\alpha/V} . \quad (37)$$

The constant α is called the coupling constant and is defined by

$$\alpha = (e^2/\epsilon \hbar) \sqrt{m/2\hbar\omega} . \quad (38)$$

This is perhaps a rather involved way of introducing the coupling constant; however, it will appear in a rather simple way later on. Note that H_{int} is proportional to α so that α is in some sense a measure of the strength of the interaction.

Recall that in the beginning of this section it was stated that the introduction of periodic boundary conditions also introduced a divergence in the energy because of the interaction among the infinite number of extra electrons in the infinite crystal. This is apparent in Equation (35) whose $k = 0$ term diverges. It can be shown that introduction of a uniform charge density to satisfy crystal neutrality cancels this diverging energy by contributing a positive energy due to the interaction between this positive charge density and the extra electrons. This is rather reminiscent of the Madelung energy whose positive terms and negative terms separately diverge but when combined yield a finite result.

Putting our modifications of the classical Hamiltonian together gives the quantal Hamiltonian (usually called the Fröhlich Hamiltonian).

$$H = \frac{\vec{p}^2}{2m} + \sum_{\vec{k}} \left[\hbar\omega b_{\vec{k}}^* b_{\vec{k}} + v_{\vec{k}} b_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} + v_{\vec{k}}^* b_{\vec{k}}^* e^{-i\vec{k} \cdot \vec{r}} \right] , \quad (39)$$

where $\vec{p}_{el}$ is now understood to be the operator

$$\vec{p}_{el} = \frac{\hbar}{i} \vec{\nabla} \quad . \quad (40)$$

In some applications it is useful to introduce Fermion operators as well as phonon operators modifying the first and last terms of Equation (39).

Weak Coupling Limit

By weak coupling it is meant that the H_{int} term on the right hand side of Equation (39) is small enough so that perturbation theory may be validly applied. Our first task is to find wave functions so that we can make a perturbation calculation.

Begin by noting that the "crystal momentum" defined by

$$\vec{p}_{op} = \vec{p}_{el} + \sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}} \quad (41)$$

is a constant of the motion. This follows at once if we can show that

$$[\vec{p}_{op} , H] = 0 \quad (42)$$

Proof of Equation (42):

By inspection $\vec{p}_{el}$ commutes with every term in H except the interaction term. Similarly $\sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}}$ commutes with everything in H except the interaction term. Thus, Equation (42) can be true only if $[\vec{p}_{el} , H_{int}]$ and $[\sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}} , H_{int}]$ are equal and opposite.

Let us compute the first commutator.

$$\begin{aligned} [\vec{p}_{el} , H_{int}] &= \left[\frac{\hbar}{i} \vec{\nabla} , \sum_{\vec{k}} \left(v_{\vec{k}} b_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} + v_{\vec{k}}^* b_{\vec{k}}^* e^{-i\vec{k} \cdot \vec{r}} \right) \right] \\ &= \sum_{\vec{k}} \hbar \vec{k} \left(v_{\vec{k}} b_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} - v_{\vec{k}}^* b_{\vec{k}}^* e^{-i\vec{k} \cdot \vec{r}} \right) \quad . \end{aligned} \quad (43)$$

The next commutator to calculate is

$$\begin{aligned}
 \left[\sum_{\vec{k}} \hbar \vec{k} \cdot \vec{b}_{\vec{k}}^* \vec{b}_{\vec{k}}, H_{\text{int}} \right] &= \sum_{\vec{m}, \vec{k}} \left[\hbar \vec{k} \cdot \vec{b}_{\vec{k}}^* \vec{b}_{\vec{k}}, \left(v_{\vec{m}} \vec{b}_{\vec{m}} e^{i\vec{m} \cdot \vec{r}} + v_{\vec{m}}^* \vec{b}_{\vec{m}}^* e^{-i\vec{m} \cdot \vec{r}} \right) \right] \\
 &= \sum_{\vec{m}, \vec{k}} \hbar \vec{k} \cdot \left(v_{\vec{m}} e^{i\vec{m} \cdot \vec{r}} \left[\vec{b}_{\vec{k}}^*, \vec{b}_{\vec{m}} \right] \vec{b}_{\vec{k}} + v_{\vec{m}}^* e^{-i\vec{m} \cdot \vec{r}} \vec{b}_{\vec{k}}^* \left[\vec{b}_{\vec{k}}, \vec{b}_{\vec{m}}^* \right] \right) \\
 &= \sum_{\vec{k}} \hbar \vec{k} \cdot \left(v_{\vec{k}}^* \vec{b}_{\vec{k}}^* e^{-i\vec{k} \cdot \vec{r}} - v_{\vec{k}} \vec{b}_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \right) .
 \end{aligned} \tag{44}$$

Note that Equations (29) and (30) were employed in the various steps in Equation (44). Since Equations (43) and (44) are equal and opposite, we have proved Equation (42).

Equation (42) allows us to use the well known theorem which states that if two operators commute we can choose eigenfunctions of one to be eigenfunctions of the other. Thus, if ψ is a wave function satisfying the eigenvalue equation

$$H \psi = E \psi , \tag{45}$$

then it will also satisfy

$$\vec{p}_{\text{op}} \psi = \vec{p} \psi , \tag{46}$$

where $\vec{p}$ is an eigenvalue.

The weak coupling limit is consistent with very low temperatures because then very few phonons are present. In the low temperature limit Equation (46) is easy to solve because

$$\vec{p}_{\text{op}} \rightarrow \vec{p}_{\text{el}} = \frac{\hbar}{i} \vec{\nabla} . \tag{47}$$

Equations (46) and (47) give at once a solution which we shall write ψ_0 to indicate it is a zero temperature solution

$$\psi_0 = \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar} \vec{p} \cdot \vec{r}} \chi_0 , \tag{48}$$

where χ_0 denotes the ground state wave function of the lattice. Since there are no phonons present

$$b_{\vec{k}} \chi_0 = 0 \quad (49)$$

From the zero phonon wave function χ_0 , one phonon wave function can be built. For example, a wave function describing the lattice with a single phonon of wave vector $\vec{k}$ can be written

$$\chi_{1,\vec{k}} = b_{\vec{k}}^* \chi_0 \quad (50)$$

For the corresponding wave function ψ , Equation (50) would suggest

$$\psi_{1,\vec{k}} = \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar} \vec{p}_{1,\vec{k}} \cdot \vec{r}} \chi_{1,\vec{k}} \quad (51)$$

Upon substitution into Equation (46), it is found that

$$\vec{p}_{1,\vec{k}} = \vec{p} - \hbar \vec{k} \quad (52)$$

In the perturbation calculations of weak coupling theory only these lowest order wave functions [Equations (48) and (51)] are used. We could keep building higher order wave functions just as we built $\psi_{1,\vec{k}}$ from ψ_0 but this would be laborious. When we get to intermediate coupling we shall see an easier way to build multi-phonon wave functions.

Thus, in the weak coupling approximation the ground state energy is given by

$$E_0 = \frac{p^2}{2m} - \sum_{\vec{k}} \frac{\left| \langle \psi_0 | H_{\text{int}} | \psi_{1,\vec{k}} \rangle \right|^2}{\left(\frac{p^2}{2m} - \frac{(\vec{p} - \hbar \vec{k})^2}{2m} - \hbar \omega \right)} \quad (53)$$

from standard perturbation theory. So explicitly calculating the matrix element we have

$$\begin{aligned} \langle \psi_0 | H_{\text{int}} | \psi_{1,\vec{k}} \rangle &= \frac{1}{V} \int d^3r d^3\rho \left\{ e^{-\frac{i}{\hbar} \vec{p} \cdot \vec{r}} \chi_0^* \right. \\ &\times \left[\sum_{\vec{m}} \left(v_{\vec{m}} b_{\vec{m}} e^{i\vec{m} \cdot \vec{r}} + v_{\vec{m}}^* b_{\vec{m}}^* e^{-i\vec{m} \cdot \vec{r}} \right) \right] b_{\vec{k}}^* \chi_0 e^{\frac{i}{\hbar} (\vec{p} - \hbar \vec{k}) \cdot \vec{r}} \left. \right\} \quad (54) \end{aligned}$$

with the r integration being over the electron coordinates and the ρ integration being over the lattice coordinates of X_0 . Employing Equations (29) and (30) in Equation (54) yields

$$\begin{aligned} \langle \Psi_0 | H_{\text{int}} | \Psi_{1,\vec{k}} \rangle &= \frac{1}{V} \int d^3\rho X_0^* v_{\vec{k}} X_0 \\ &= v_{\vec{k}} \left\{ \int d^3\rho X_0^* X_0 \right\} \frac{1}{V} = v_{\vec{k}} \end{aligned} \quad (55)$$

where the final step follows from the normalization of the function X_0 .

From Equations (55) and (53) we get for the ground state energy

$$E_0 = \frac{p^2}{2m} - \sum_{\vec{k}} \frac{|v_{\vec{k}}|^2}{\left(\hbar\omega + \frac{\hbar^2 k^2}{2m} - \frac{\hbar\vec{k} \cdot \vec{p}}{m} \right)} \quad (56)$$

To make further progress we can go to a continuum approximation via

$$\frac{1}{V} \sum_{\vec{k}} \rightarrow \frac{1}{(2\pi)^3} \int d^3k \quad (57)$$

which is quite consistent with our derivation of a macroscopic Hamiltonian and the subsequent weak coupling and low temperature limit. In the continuum approximation substitution of Equation (37) into Equation (56) yields to first order in p^2

$$E_0 = \frac{p^2}{2m} - \frac{\alpha}{6} \frac{p^2}{2m} - \alpha\hbar\omega \quad (58)$$

We interpret the $-\alpha\hbar\omega$ as a binding energy of the polaron. If we combine the terms in p^2 we may define an effective polaron mass m^* by writing

$$E_0 = \frac{p^2}{2m^*} - \alpha\hbar\omega \quad ; \quad (59)$$

that is, with

$$m^* = \frac{m}{1 - \alpha/6} \quad (60)$$

If we look at the wave functions employed in this perturbation calculation we note that the more complicated wave function was $\Psi_{1,\vec{k}}$ but

but it allows only one phonon in the whole crystal! This is not very realistic and it is precisely this difficulty that intermediate coupling theory cures. But before we go on to that theory, it is of interest to calculate (by using the phonon number operator and the perturbed wave function) how many phonons exist in the crystal. We shall see that this gives a rough idea for what range of α weak coupling theory is adequate.

We define the average number of phonons in the crystal by

$$N_{Av} = \langle \Psi | \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} | \Psi \rangle, \quad (61)$$

where Ψ is the perturbed wave function

$$\Psi = \Psi_0 - \sum_{\vec{k}} \frac{V_{\vec{k}} \Psi_{1,\vec{k}}}{\left\{ \hbar\omega + \frac{\hbar^2 k^2}{2m} - \frac{\hbar \vec{k} \cdot \vec{p}}{m} \right\}} \quad (62)$$

Going to the continuum limit as we did for Equation (58) yields

$$N_{Av} = \frac{\alpha}{2} \left\{ 1 + \frac{p^2}{4m\hbar\omega} \right\} \quad (63)$$

in the limit of low p . Thus, $\alpha/2$ is a rough estimate of the number of phonons.

To be consistent with our choice of wave functions we must have $\alpha \leq 2$.

Pines⁽⁸⁾ concludes that a perturbation approach is appropriate for $\alpha \geq \frac{1}{2}$ and gets in trouble for $\alpha \geq 2$.

What values of α do typical insulators have? From Equations (38) and (A10) we have

$$\alpha = \frac{e^2}{\hbar} \frac{\epsilon_s - \epsilon_\infty}{\epsilon_s \epsilon_\infty} \sqrt{\frac{m}{2\hbar\omega}} \quad (64)$$

Experimental values are hard to come by for many of these values, particularly high temperature values. If we substitute for ω from the Lydanne-Sachs-Teller relation

$$\omega = \omega_r \sqrt{\epsilon_s / \epsilon_\infty} \quad (65)$$

where ω_r is the restrahl frequency, we obtain

$$\alpha = \frac{e^2}{\hbar} \left(\frac{\epsilon_s - \epsilon_\infty}{\epsilon_s \epsilon_\infty} \right) \sqrt{\frac{m}{2\hbar\omega_r}} \left(\epsilon_\infty / \epsilon_s \right)^{1/4} \quad (66)$$

For most materials, the parameters necessary to calculate α by Equation (66) are not experimentally known over a wide temperature range. Some data exists for the effective mass⁽¹¹⁾ of various halides, but we have not found other results. A similar situation exists for ϵ_s and ϵ_∞ . Although some experimental⁽¹²⁾ and theoretical⁽¹³⁾ work has been done on the temperature dependence of the dielectric constant a sizeable amount of work must be done before values of α for many materials and a broad temperature range will exist.

Intermediate Coupling

The intermediate coupling method is a variational technique. The Fröhlich Hamiltonian is subjected to two successive transformations. The first transformation removes the electron coordinate. The second transformation employs the variational technique to get rid of terms linear in $b_{\vec{k}}$ and $b_{\vec{k}}^*$.

Let us first make the transformation which removes the electron coordinate from the Hamiltonian. We are in disagreement here with Section 2.1 of Pines⁽⁸⁾ but since the end result is the same, it is probably a disagreement based on misprints.

We wish to apply a transformation generated by

$$u_1 = \exp \left(-i \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) \quad (67)$$

Writing the eigenvalue equation for the Fröhlich Hamiltonian as

$$H \psi = E \psi \quad , \quad (68)$$

then the new Hamiltonian

$$H = u_1^{-1} H u_1 \quad (69)$$

will obey the eigenvalue equation

$$H \phi = E \phi \quad (70)$$

with

$$\phi = U_1^{-1} \psi \quad (71)$$

To calculate $U_1^{-1} H U_1$ we must find $U_1^{-1} \vec{p}_{el} U_1$ and $U_1^{-1} b_{\vec{k}} U_1$. The first is easy. From Equations (67) and (40), we have at once

$$U_1^{-1} \vec{p}_{el} U_1 = \vec{p}_{el} - \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} \hbar \vec{k} \quad (72)$$

In calculating $U_1^{-1} b_{\vec{k}} U_1$ we recall that $b_{\vec{k}}$ commutes with $b_{\vec{m}}$ and $b_{\vec{m}}^*$ if $\vec{m} \neq \vec{k}$ so we can write

$$\begin{aligned} U_1^{-1} b_{\vec{k}} U_1 &= \exp \left(i \sum_{\vec{m}} b_{\vec{m}}^* b_{\vec{m}} \vec{k} \cdot \vec{r} \right) b_{\vec{k}} \exp \left(-i \sum_{\vec{m}} b_{\vec{m}}^* b_{\vec{m}} \vec{k} \cdot \vec{r} \right) \\ &= \exp \left(i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) b_{\vec{k}} \exp \left(-i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) \end{aligned} \quad (73)$$

We next expand the right hand exponential, multiply by the preceeding $b_{\vec{k}}$, and rearrange as follows:

$$\begin{aligned} U_1^{-1} b_{\vec{k}} U_1 &= \exp \left(i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) b_{\vec{k}} \left(1 - i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} + \dots \right) \\ &= \exp \left(i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) \left(b_{\vec{k}} - i b_{\vec{k}}^* b_{\vec{k}} b_{\vec{k}} \vec{k} \cdot \vec{r} + \dots \right) \\ &= \exp \left(i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) \left(1 - i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} + \dots \right) b_{\vec{k}} \\ &= \exp \left(i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) \exp \left(-i b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) \\ &= \exp \left(-i \vec{k} \cdot \vec{r} \left[b_{\vec{k}}, b_{\vec{k}}^* \right] \right) b_{\vec{k}} = e^{-i \vec{k} \cdot \vec{r}} b_{\vec{k}} \end{aligned} \quad (74)$$

where in the last step we used Equation (29). The conjugate transpose of Equation (74) is

$$U_1^{-1} b_{\vec{k}}^* U_1 = e^{i \vec{k} \cdot \vec{r}} b_{\vec{k}}^* \quad (75)$$

From Equations (39), (69), (72), (74) and (75) we have the new Hamiltonian

$$H = \frac{(\vec{p}_{e1} - \sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}})^2}{2m} + \sum_{\vec{k}} \hbar \omega b_{\vec{k}}^* b_{\vec{k}} + \sum_{\vec{k}} (v_{\vec{k}} b_{\vec{k}} + v_{\vec{k}}^* b_{\vec{k}}^*) \quad (76)$$

Note that the electron coordinate has disappeared in the interaction term by virtue of Equations (74) and (75). As a consequence, $\vec{p}_{e1}$ is a constant of the motion and can be replaced by its eigenvalue which we now compute. Our wave function in the new representation is ϕ so we calculate

$$\begin{aligned} \vec{p}_{e1} \phi &= \vec{p}_{e1} U_1^{-1} \psi \\ &= \frac{\hbar}{i} \vec{\nabla} \exp \left(i \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right) \psi \\ &= U_1^{-1} \left(\vec{p}_{e1} + \sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}} \right) \psi \\ &= U_1^{-1} \vec{p}_{op} \psi = U_1^{-1} \vec{p} \psi = \vec{p} \phi, \end{aligned} \quad (77)$$

where we have used Equations (67) and (46).

Thus, the eigenvalue of $\vec{p}_{e1}$ in the ϕ representation is $\vec{p}$ which was the eigenvalue of $\vec{p}_{op}$ in the ψ representation. Combining Equations (77) and (76) yields

$$H = \frac{(\vec{p} - \sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}})^2}{2m} + \sum_{\vec{k}} \hbar \omega b_{\vec{k}}^* b_{\vec{k}} + \sum_{\vec{k}} (v_{\vec{k}} b_{\vec{k}} + v_{\vec{k}}^* b_{\vec{k}}^*) \quad (78)$$

an equation with no operators except the boson creation and annihilation operators for the phonons.

The next transformation to be applied will give a much more complicated Hamiltonian but will have the virtue of removing terms linear in $b_{\vec{k}}$ and $b_{\vec{k}}^*$

so that perturbation theory may be applied. Consider, then, the transformation generated by

$$U_2 = \exp \left\{ \sum_{\vec{k}} \left(b_{\vec{k}}^* f(\vec{k}) - b_{\vec{k}} f^*(\vec{k}) \right) \right\} , \quad (79)$$

where $f(\vec{k})$ is some function of $\vec{k}$ to be determined in a variational calculation of the ground state energy of the resulting Hamiltonian.

This new Hamiltonian is given by

$$H' = U_2^{-1} H U_2 , \quad (80)$$

so from Equation (70) we can say that H' will obey an eigenvalue equation

$$H' \Gamma = E \Gamma , \quad (81)$$

where the new wave functions are given by

$$\Gamma = U_2^{-1} \Phi . \quad (82)$$

To explicitly carry out the calculation of the right hand side of Equation (80), we must compute $U_2^{-1} b_{\vec{k}} U_2$ (and $U_2^{-1} b_{\vec{k}}^* U_2$).

The computation of $U_2^{-1} b_{\vec{k}} U_2$ involves the algebraic identity

$$e^{-S} A e^S = A + [A, S] + \frac{1}{2!} [[A, S], S] + \dots \quad (83)$$

The nice thing about this equation is that for our case $[A, S]$ will be a constant so that all terms to its right vanish. For our case, we have

$$\begin{aligned} U_2^{-1} b_{\vec{k}} U_2 &= b_{\vec{k}} + \left[b_{\vec{k}} , \sum_{\vec{m}} \left(b_{\vec{m}}^* f(\vec{m}) - b_{\vec{m}} f^*(\vec{m}) \right) \right] \\ &= b_{\vec{k}} + \sum_{\vec{m}} f(\vec{m}) \left[b_{\vec{k}} , b_{\vec{m}}^* \right] \\ &= b_{\vec{k}} + f(\vec{k}) , \end{aligned} \quad (84)$$

again using Equation (29).

By taking the transpose conjugate of Equation (84), we find how $b_{\vec{k}}^*$ transforms,

$$U_2^{-1} b_{\vec{k}}^* U_2 = b_{\vec{k}}^* + f^*(\vec{k}) . \quad (85)$$

Equations (84) and (85) are all we need to know to calculate H^1 via Equations (80) and (78).

The result is

$$H^1 = H_0 + H_1, \quad (86)$$

where

$$\begin{aligned} H_0 = & \frac{(\vec{p} - \sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}})^2}{2m} + \sum_{\vec{k}} [v_{\vec{k}} f(\vec{k}) + v_{\vec{k}}^* f^*(\vec{k})] \\ & + \frac{\hbar^2}{2m} \left[\sum_{\vec{k}} |f(\vec{k})|^2 \vec{k} \right]^2 + \sum_{\vec{k}} |f(\vec{k})|^2 \left(\hbar \omega - \frac{\hbar \vec{k} \cdot \vec{p}}{m} + \frac{\hbar^2 k^2}{2m} \right) \\ & + \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} \frac{\hbar^2 \vec{k}}{m} \cdot \sum_{\vec{m}} |f(\vec{m})|^2 \vec{m} + \sum_{\vec{k}} \hbar \omega b_{\vec{k}}^* b_{\vec{k}} \\ & + \sum_{\vec{k}} \left\{ b_{\vec{k}}^* v_{\vec{k}} + b_{\vec{k}} v_{\vec{k}} \right. \\ & \left. + (b_{\vec{k}}^* f(\vec{k}) + b_{\vec{k}} f^*(\vec{k})) \left(\hbar \omega - \frac{\hbar \vec{k} \cdot \vec{p}}{m} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 \vec{k}}{m} \cdot \sum_{\vec{m}} |f(\vec{m})|^2 \vec{m} \right) \right\} \quad (87) \end{aligned}$$

and

$$\begin{aligned} H_1 = & \frac{\hbar^2}{2m} \sum_{\vec{m}, \vec{k}} \vec{m} \cdot \vec{k} \left\{ b_{\vec{k}}^* b_{\vec{m}} f^*(\vec{k}) f^*(\vec{m}) + b_{\vec{k}}^* b_{\vec{m}}^* f(\vec{k}) f(\vec{m}) \right. \\ & \left. + 2 b_{\vec{k}}^* b_{\vec{m}} f(\vec{k}) f^*(\vec{m}) \right\} \\ & + \frac{\hbar^2}{m} \sum_{\vec{k}, \vec{m}} \vec{m} \cdot \vec{k} \left\{ b_{\vec{k}}^* b_{\vec{k}} b_{\vec{m}}^* f^*(\vec{m}) + b_{\vec{m}}^* b_{\vec{k}}^* b_{\vec{k}} f(\vec{m}) \right\} \quad (88) \end{aligned}$$

Notice the terms in H_0 that are linear in $b_{\vec{k}}$ and $b_{\vec{k}}^*$. We now calculate the ground state energy for a choice of trial function r . The subsequent minimization of this ground state energy with respect to $f(\vec{k})$ determines $f(\vec{k})$ and destroys these linear terms.

Let us now perform the variational calculation. Our choice of trial function is the vacuum state with no phonons present, i.e.,

$$\Gamma = |0\rangle. \quad (89)$$

Thus, the ground state energy is less than

$$E = \langle 0 | H' | 0 \rangle. \quad (90)$$

Remembering that a destruction operator operating on $|0\rangle$ gives zero, we have from Equations (86), (87), (88), and (90)

$$E = \frac{p^2}{2m} + \sum_{\vec{k}} \left\{ v_{\vec{k}} f(\vec{k}) + v_{\vec{k}}^* f^*(\vec{k}) \right\} + \frac{\hbar^2}{2m} \left[\sum_{\vec{k}} |f(\vec{k})|^2 \right]^2 + \sum_{\vec{k}} \left\{ \hbar\omega - \frac{\hbar\vec{k}}{m} \cdot \vec{p} + \frac{\hbar^2 k^2}{2m} \right\} |f(\vec{k})|^2, \quad (91)$$

where we have also used the orthogonality of the vacuum state and the one and two phonon states.

The variational theorem says that if we minimize E with respect to the unknown parameters $f(\vec{k})$ and $f^*(\vec{k})$ then we have an upper bound for the ground state energy.

We now minimize via

$$\partial E / \partial f^*(\vec{k}) = \partial E / \partial f(\vec{k}) = 0 \quad (92)$$

obtaining the minimization condition

$$v_{\vec{k}} + f^*(\vec{k}) \left[\frac{\hbar^2 k^2}{2m} + \hbar\omega - \frac{\hbar\vec{k}}{m} \cdot \vec{p} + \frac{\hbar^2 \vec{k}}{m} \cdot \sum_{\vec{m}} |f(\vec{m})|^2 \vec{m} \right] \quad (93)$$

and the complex conjugate equation.

Combining Equations (91) and (93) yields the minimized energy

$$E = \frac{p^2}{2m} + \sum_{\vec{k}} v_{\vec{k}}^* f^*(\vec{k}) - \frac{\hbar^2}{2m} \sum_{\vec{k}} f^*(\vec{k}) \left\{ \sum_{\vec{m}} |f(\vec{m})|^2 \vec{m} \right\}^2. \quad (94)$$

Combining Equations (87) and (93) gives

$$H_0 = \frac{\left(\vec{p} - \sum_{\vec{k}} \hbar \vec{k} b_{\vec{k}}^* b_{\vec{k}} \right)^2}{2m} + \sum_{\vec{k}} v_{\vec{k}}^* f^*(\vec{k}) - \frac{\hbar^2}{2m} \left\{ \sum_{\vec{k}} \left| f(\vec{k}) \right|^2 \vec{k} \right\}^2 + \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} \frac{\hbar^2 \vec{k}}{m} \cdot \sum_{\vec{m}} \left| f(\vec{m}) \right|^2 \vec{m} \quad (95)$$

Note that H_0 is now diagonal. For higher order contributions, H_1 is treated as a perturbation. This is justified at low temperatures because few phonons are present and H_1 is quadratic and cubic in the phonon operators.

It is perhaps worth commenting on what may seem to be a slight ambiguity. Earlier we stated that in this intermediate coupling section we would perform a variational calculation with a multi-phonon wave function yet we made the choice of trial function given in Equation (89). This ambiguity disappears if we return to the original (Ψ) representation. In particular, we want given by

$$\langle 0 | H' | 0 \rangle = \langle \Psi | H | \Psi \rangle \quad (96)$$

This is straightforward because by Equations (89), (82), (80), (71) and (69) we can proceed as follows:

$$\begin{aligned} \langle 0 | H' | 0 \rangle &= \langle 0 | U_2^{-1} H U_2 | 0 \rangle \\ &= \langle 0 | U_2^{-1} U_1^{-1} H U_1 U_2 | 0 \rangle \\ &= \langle \Psi | H | \Psi \rangle \quad , \end{aligned} \quad (97)$$

where

$$\begin{aligned} \Psi &= U_1 U_2 | 0 \rangle \\ &= \exp \left[-i \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} \vec{k} \cdot \vec{r} \right] \exp \left[\sum_{\vec{k}} \left(b_{\vec{k}}^* f(\vec{k}) - b_{\vec{k}} f^*(\vec{k}) \right) \right] | 0 \rangle \quad (98) \end{aligned}$$

Hence, the choice of trial function $|0\rangle$ in the Γ representation corresponds to the multiphonon trial function of Equation (98) in the Ψ representation.

To see how intermediate coupling theory compares with weak coupling theory it is instructive to calculate the polaron mass and the number of phonons and match these results against Equations (60) and (63).

There is an immediate difficulty because looking back at Equation (93) we see that the minimization condition cannot be solved for $f(\vec{k})$ in a closed form. In particular, $f(\vec{k})$ cannot be easily removed from Equation (94). Pines⁽⁸⁾ has a clever way around this difficulty by noting that since $\vec{p}$ is the only preferred direction in the problem symmetry demands that

$$\sum_{\vec{k}} |f(\vec{k})|^2 \hbar \vec{k} = \eta \vec{p} \quad , \quad (99)$$

where η is a constant of proportionality.

Applying Equation (99) to Equation (93) and solving for $f(\vec{k})$ gives

$$f(\vec{k}) = \frac{-v_{\vec{k}}^*}{\left\{ \hbar \omega + \frac{\hbar^2 k^2}{2m} - \frac{\hbar \vec{k}}{m} \cdot \vec{p} [1 - \eta] \right\}} \quad . \quad (100)$$

and hence from Equations (99) and (100)

$$\eta \vec{p} = \sum_{\vec{k}} \frac{|v_{\vec{k}}|^2 \hbar \vec{k}}{\left\{ \hbar \omega + \frac{\hbar^2 k^2}{2m} - \frac{\hbar \vec{k}}{m} \cdot \vec{p} [1 - \eta] \right\}^2} \quad . \quad (101)$$

Substitution of Equation (37) for $v_{\vec{k}}$ into Equation (101) and making the continuum approximation via Expression (57) yields

$$[1 - \eta]^2 \eta = \frac{\alpha}{2} \left(\frac{2m \hbar \omega}{p^2} \right)^{3/2} \left(\sin^{-1} q - \frac{q}{\sqrt{1 - q^2}} \right) \quad , \quad (102)$$

where

$$q = [1 - \eta] \sqrt{p^2 / 2m \hbar \omega} \quad (103)$$

In the limit of small P Equation (102) straightforwardly gives

$$\eta = \frac{\alpha}{6 + \alpha} \quad . \quad (104)$$

Making the continuum approximation in Equation (94) and using Equation (99) results in

$$E = \frac{p^2}{2m} \left[1 - \eta^2 \right] - \frac{\alpha \hbar \omega \sin^{-1} q}{q} \quad (105)$$

Taking the small P limit of the energy equation and substituting for η from Equation (104) yields

$$E = \frac{p^2}{2m} \frac{1}{1 + \alpha/6} - \alpha \hbar \omega \quad (106)$$

to lowest order in p^2 . Proceeding as we did to obtain Equation (60) we define the polaron mass as

$$m^* = m \left[1 + \alpha/6 \right] \quad (107)$$

Note that in the limit of small α Equations (60) and (107) are the same.

We now sketch a similar calculation for the average number of phonons which is given by

$$\begin{aligned} N_{Av} &= \langle \psi \left| \sum_{\vec{k}} b_{\vec{k}}^* b_{\vec{k}} \right| \psi \rangle = \sum_{\vec{k}} \langle 0 \left| U_2^{-1} U_1^{-1} b_{\vec{k}}^* b_{\vec{k}} U_1 U_2 \right| 0 \rangle \\ &= \sum_{\vec{k}} \langle 0 \left| U_2^{-1} b_{\vec{k}}^* b_{\vec{k}} U_2 \right| 0 \rangle = \sum_{\vec{k}} \left| f(\vec{k}) \right|^2 \\ &= \sum_{\vec{k}} \frac{|\vec{v}_{\vec{k}}|^2}{\left\{ \hbar \omega + \frac{\hbar^2 k^2}{2m} - \frac{\hbar \vec{k} \cdot \vec{p}}{m} [1 - \eta] \right\}^2} \quad (108) \end{aligned}$$

where we have employed Equations (71), (82), (74), (75), (84), (85), and (100).

Again going to the continuum limit we obtain

$$N_{Av} = \frac{\alpha}{2} \left\{ 1 + \frac{1}{\left(1 + \alpha/6 \right)^2} \frac{p^2}{4m\hbar\omega} \right\} \quad (109)$$

to lowest order in p^2 . Comparison of Equations (63) and (109) indicate that they are the same in the limit of small α but otherwise Equation (63) gives a larger result.

Pines⁽⁸⁾ has estimated the validity range of intermediate coupling theory by applying perturbation theory with H_1 as the perturbation. He concludes that intermediate coupling is valid for $\alpha \leq 3$ finding that at $\alpha = 3$ H_1 alters E by approximately 6%. Other authors,^(6,9) uninhibited by Pines' modesty, say the validity range may be extended nearly to $\alpha = 6$.

Finally, it should be pointed out that work on the kinetics of the polaron in this limit has been done^(14,15) but neither time nor space allows us to describe these results in this introductory review. The methods of weak and intermediate polaron theory are also of use in treatments of systems consisting of a mixture of bosons and dilute fermions; e.g., mixtures on ^3He in superfluid ^4He .⁽¹⁶⁾

THEORY OF SMALL POLARONS

When the electron and lattice are strongly coupled the polaron exists in a highly localized state in which the electron is bound to a positive ion site and is surrounded by the lattice polarization it has induced. The highly localized nature of the electron keeps the polaron size to the order of the lattice spacing and, hence, the term "small" polaron is used.

The small polaron may move from its localized site either by tunneling or by phonon activated jumps. This was first realized by Yamashita and Kurosawa.^(17,18) A very careful paper by Holstein⁽¹⁹⁾ corrected some errors in the work of Yamashita and Kurosawa. Other formulations⁽²⁰⁻²⁵⁾ recover the essential mechanisms of tunneling and hopping although differing in detail.

It is found that below a critical temperature the tunneling process is dominant while above this temperature the hopping mechanism predominates. The critical temperature is on the order of half the Debye temperatures.⁽¹⁹⁾

The hopping mechanism at high temperatures would appear to be a classical effect and this is the approach taken by Sewell.^(22,26) We shall follow through Sewell's approach. This approach is somewhat phenomenological and the model is really made to fit Holstein's approach; however, the Sewell attack is much quicker and gives the usual result.

Sewell begins by recasting previous formalisms in a form which leads easily to his model. He then states the elements of his model and follows through to obtain a conductivity characteristic of the hopping mechanism.

Sewell Version of Other Theories

We write the Hamiltonian again as a sum of three pieces

$$H = H_{el} + H_{ph} + H_{int} \quad (110)$$

and as before H_{el} is the energy of the electron in a rigid lattice, H_{ph} is the energy associated with lattice vibration, and H_{int} takes account of the interactions between the vibrational lattice modes and the electron.

The localized nature of the electron suggests that we use a tight binding approach building wave functions from the set of mutually orthogonal localized electronic states, $\psi_{\alpha}(\vec{x})$, centered on positive ion sites $\vec{a}_{\alpha}$ with $\vec{x}$ being the electron position. It is convenient to employ Fermion creation and annihilation operators c_{α}^* , c_{α} for these states.

In Appendix B we show that

$$H_{el} = \sum_{\alpha} E_{\alpha} c_{\alpha}^* c_{\alpha} + \sum_{\alpha \neq \beta} J_{\alpha\beta} c_{\alpha}^* c_{\beta} \quad , \quad (111)$$

where the sums are over positive ion sites. Note that the first piece of H_{el} is diagonal while the second piece involves transitions from ion β to ion α , transitions induced by the static interaction between the electron and the rigid lattice.

The vibrational part of the Hamiltonian is written

$$H_{ph} = \frac{1}{2} \sum_{\lambda} \left[p_{\lambda}^2 + \omega_{\lambda}^2 q_{\lambda}^2 \right] \quad (112)$$

Some treatments⁽²⁷⁾ quantize Equation (112) in terms of the phonon creation and annihilation operators but we are interested in high temperatures and will eventually replace the phonon field with a temperature reservoir.

The interaction term, H_{int} , is assumed to be linear in the generalized ion coordinates Q_{λ} . This is an assumption that is essentially the same as made in building the Fröhlich Hamiltonian since we are considering the interaction of the electron with the polarization field and neglecting any higher order (multipole) effects. H_{int} has both a local and a non-local piece so we write

$$H_{int} = H'_{int} + H''_{int} \quad (113)$$

where

$$H'_{int} = \sum_{\alpha, \lambda} K_{\alpha\lambda} c_{\alpha}^* c_{\alpha} Q_{\lambda} \quad (114)$$

and

$$H''_{int} = \sum_{\substack{\alpha, \beta, \lambda \\ \alpha \neq \beta}} L_{\alpha\beta\lambda} c_{\alpha}^* c_{\beta} Q_{\lambda} \quad (115)$$

The coefficients $K_{\alpha\lambda}$, $L_{\alpha\beta\lambda}$ contain the finer details of the model which we do not need to consider here.

The non-local piece, H''_{int} , governs processes involving transfer of the electron from one site to another. Since these transitions result from the interaction we call them phonon induced jumps. On the other hand, H'_{int} , the local piece, governs the properties of the electron while it remains on its site. This latter term then must take care of the local polarization of the lattice induced by the electron on its site.

We now introduce a transformation which will result in a form which will allow us to explicitly define the polaron. The new Hamiltonian will be

$$H = e^{-B} H e^B, \quad (116)$$

where

$$B = \frac{i}{\hbar} \sum_{\alpha, \lambda} c_{\alpha}^* c_{\alpha} \frac{K_{\alpha\lambda}}{\omega_{\lambda}} p_{\lambda}. \quad (117)$$

The transformation is somewhat involved and appears in Appendix C. The result is

$$H = H_0 + H_{ph} + H_1 + H_2 \quad (118)$$

where

$$H_0 = \sum_{\alpha} \epsilon_{\alpha}' c_{\alpha}^* c_{\alpha} \quad (119)$$

with

$$\epsilon_{\alpha}' = \epsilon_{\alpha} - \frac{1}{2} \sum_{\lambda} \left(K_{\alpha\lambda} / \omega_{\lambda} \right)^2. \quad (120)$$

H_0 is the renormalized energy for the polaron as explained in Appendix C and c_{α}^* , c_{α} are now to be interpreted as creation, annihilation operators for the polaron rather than the electron. H_{ph} is defined by

$$H_{ph} = \frac{1}{2} \sum_{\lambda} \left(p_{\lambda}^2 + \omega_{\lambda}^2 q_{\lambda}^2 \right), \quad (121)$$

and

$$H_1 + H_2 = \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \frac{\hbar}{2} K_{\alpha\beta} (P, Q) c_{\alpha}^* c_{\beta} \quad (122)$$

with

$$\begin{aligned} & \frac{\hbar}{2} K_{\alpha\beta} (P, Q) \\ &= \exp \left[-\frac{i}{\hbar} \sum_{\gamma} \frac{K_{\alpha\gamma}}{\omega_{\gamma}} p_{\gamma} \right] (J_{\alpha\beta} + \sum_{\lambda} L_{\alpha\beta\lambda} q_{\lambda}) \exp \left[\frac{i}{\hbar} \sum_{\gamma} \frac{K_{\beta\gamma}}{\omega_{\gamma}} p_{\gamma} \right] \end{aligned} \quad (123)$$

The reason for writing the left hand side of Equation (122) in two parts will become apparent in the following paragraph.

Since H_1 and H_2 only involve products of the form $c_{\alpha}^* c_{\beta}$ for $\alpha \neq \beta$ they must govern processes which transfer the polaron from one site to another. We shall introduce a thermal average so that H_1 will govern tunneling processes. H_2 will be everything left over and will, therefore, govern the jumping mechanism. To decide how to define the thermal average we must

recall that by tunneling we mean transitions that leave the lattice unchanged. The neat thing to do is to think of solving the eigenvalue problem for H_{ph} along and arriving at a set of orthonormal eigenfunctions, say ϕ_n . We now define H_1 by

$$H_1 = \frac{\hbar}{2} \sum_{\alpha, \beta} \Omega_{\alpha\beta} c_{\alpha}^* c_{\beta} \quad , \quad (124)$$

where

$$\Omega_{\alpha\beta} = \langle K_{\alpha\beta} (P, Q) \rangle \quad , \quad (125)$$

the brackets meaning the thermal average defined by

$$\langle K_{\alpha\beta} \rangle = \frac{\sum_n \langle \phi_n | K_{\alpha\beta} e^{-\beta H_{ph}} | \phi_n \rangle}{\sum_n \langle \phi_n | e^{-\beta H_{ph}} | \phi_n \rangle} \quad , \quad (126)$$

$$\text{Where } \beta = 1/kT, \quad (127)$$

T being the temperature and k being the Boltzman constant. This definition of H_1 guarantees that it governs only processes which leave the lattice phonons uninvolved because of the orthonormality of the ϕ_n .

H_2 is whatever is left over and by Equations (122) and (124) must, therefore, be

$$H_2 = \frac{\hbar}{2} \sum_{\alpha, \beta} \left\{ K_{\alpha\beta} (P, Q) - \Omega_{\alpha\beta} \right\} c_{\alpha}^* c_{\beta} \quad . \quad (128)$$

Because $J_{\alpha\beta}$ and $L_{\alpha\beta\gamma}$ involve overlap integrals the sum $H_1 + H_2$ is small⁽¹⁹⁾ for strong coupling where the tight binding approach is appropriate. Thus, the transformed Hamiltonian is somewhat tractable. However, it is the mathematical complexity of H_2 which motivated the alternate classical approach by Sewell which is the subject of the next section.

However, before we begin the next section we shall modify what we now have slightly so that the Sewell model will follow easily. This modification

is appropriate at high temperatures when the phonon coordinates Q_λ and momenta P_λ may be treated classically. The classical time dependent variables corresponding to P_λ and Q_λ are

$$Q_\lambda(t) = Q_\lambda \cos \omega_\lambda t + \frac{P_\lambda}{\omega_\lambda} \sin \omega_\lambda t$$

$$P_\lambda(t) = P_\lambda \cos \omega_\lambda t - \omega_\lambda Q_\lambda \sin \omega_\lambda t \quad . \quad (129)$$

The effect of the polaron-lattice induced jumps will still be given by H_2 but with P_λ and Q_λ replaced by the time dependent variables of Equation (129). Thus, the quantum mechanical phonon field is replaced by a fluctuating thermal field. The Hamiltonian becomes

$$H' = H_0 + H_1 + H'_2 \quad (130)$$

with

$$H'_2 = \frac{\hbar}{2} \sum_{\alpha \neq \beta} F_{\alpha\beta}(t) c_\alpha^* c_\beta \quad , \quad (131)$$

where

$$F_{\alpha\beta}(t) = K_{\alpha\beta}(P(t), Q(t)) - \langle K_{\alpha\beta}(P(t), Q(t)) \rangle \quad . \quad (132)$$

Although we have explicitly dropped H_{ph} it determines the statistical properties of $P(t)$ and $Q(t)$ which in turn govern the statistical properties of $F_{\alpha\beta}(t)$. One fact that we shall use later follows from Equation (132) and that is

$$\langle F_{\alpha\beta}(t) \rangle = 0 \quad . \quad (133)$$

When we get to the Sewell model we shall be interested in a conductivity and, hence, shall consider applying an electric field to the sample. The contribution to the Hamiltonian of particular interest will be the dipole operator of the electron dotted into the electric field.

We shall at that point want the dipole operator expressed in terms of the fermion operators. If the electron position is $\vec{x}$ then the classical dipole is $-e_0 \vec{x}$ with $-e_0$ being the electronic charge. The corresponding operator is (following Appendix B)

$$\begin{aligned} \vec{m} &= \left\langle \sum_{\alpha} c_{\alpha} \psi_{\alpha} \left| -e_0 \vec{x} \right| \sum_{\beta} c_{\beta} \psi_{\beta} \right\rangle \\ &= -e_0 \sum_{\alpha, \beta} c_{\alpha}^* c_{\beta} \left\langle \psi_{\alpha}(\vec{x}) \left| \vec{x} \right| \psi_{\beta}(\vec{x}) \right\rangle \end{aligned} \quad (134)$$

For simplicity we assume that the ψ_{α} and ψ_{β} are S states so the integral as carried out in Appendix B yields for $\vec{m}$

$$\vec{m} = -e_0 \sum_{\alpha} c_{\alpha}^* c_{\alpha} \vec{a}_{\alpha} \quad (135)$$

The Sewell Model

This model consists of a single polaron which is highly localized but may move among its possible sites by either tunneling or hopping. The piece of the Hamiltonian which governs tunneling is labeled H_1 and is chosen to be the same as H_1 of Equation (124). The Sewell modification is to assume that the hopping mechanism is governed by an interaction H_2^I which is not identical to H_2^I of Equation (131) but preserves its gross features. In analogy with Equation (131) we write

$$H_2^I = \frac{\hbar}{2} \sum_{\alpha, \beta} F_{\alpha\beta}(t) c_{\alpha}^* c_{\beta} \quad (136)$$

However, we do not define $F_{\alpha\beta}(t)$ in detail but give only its statistical properties. These properties will determine the influence of the thermal reservoir (the classical replacement of the phonons) on the polaron.

We now write down the statistical properties of $F_{\alpha\beta}(t)$ and will then attempt to justify them. We have

$$\langle F_{\alpha\beta}(t) \rangle = 0 \quad (137)$$

$$\langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_2) \rangle = f_{\alpha\beta}(|t_1 - t_2|) \quad (138)$$

$$\langle F_{\alpha\beta}(t_1) \dots F_{\alpha\beta}(t_{2n+1}) \rangle = 0 \quad (139)$$

$$\begin{aligned} & \langle F_{\alpha\beta}(t_1) \dots F_{\alpha\beta}(t_{2n}) \rangle \\ &= \sum_{i,j} \prod_{i,j} \langle F_{\alpha\beta}(t_i) F_{\alpha\beta}(t_j) \rangle, \end{aligned} \quad (140)$$

where n is a positive integer and $f_{\alpha\beta}(|t_1 - t_2|)$ is a decreasing function of $|t_1 - t_2|$ of which we shall speak further.

Equation (137) is written in strict analogy with Equation (133) since we wish to preserve the gross features of H_2' . Since $f_{\alpha\beta}(|t_1 - t_2|)$ decreases with time $|t_1 - t_2|$ Equation (138) for the "autocorrelation" function is consistent with Equation (137). In particular, we think of $f_{\alpha\beta}(t)$ as having a decay time τ so that if $|t_1 - t_2| \gg \tau$ the functions on the left hand side of Equation (138) become uncorrelated and Equation (137) applies. The only simpler expression would be to set the right hand side of Equation (138) equal to zero but this gives a trivial result. Equation (139) says that no more than two times can fall within the correlation time τ . Thus, a product of three functions within the thermal average could have at most two correlated functions so we might write

$$\begin{aligned} & \langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_2) F_{\alpha\beta}(t_3) \rangle \\ &= \langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_2) \rangle \langle F_{\alpha\beta}(t_3) \rangle \\ &+ \langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_3) \rangle \langle F_{\alpha\beta}(t_2) \rangle \\ &+ \langle F_{\alpha\beta}(t_2) F_{\alpha\beta}(t_3) \rangle \langle F_{\alpha\beta}(t_1) \rangle = 0 \end{aligned} \quad (141)$$

by Equation (137). Continuing the argument would work for any odd number of functions within the average brackets because there would always be one uncorrelated function left over to which Equation (137) applies. A very similar argument relates Equation (140) back to Equation (138). To see

what $\sum_{i,j} \prod$ in Equation (140) means we consider a specific example; i.e., let $n = 2$ to write

$$\begin{aligned}
 & \langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_2) F_{\alpha\beta}(t_3) F_{\alpha\beta}(t_4) \rangle \\
 &= \langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_2) \rangle \langle F_{\alpha\beta}(t_3) F_{\alpha\beta}(t_4) \rangle \\
 &+ \langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_3) \rangle \langle F_{\alpha\beta}(t_2) F_{\alpha\beta}(t_4) \rangle \\
 &+ \langle F_{\alpha\beta}(t_1) F_{\alpha\beta}(t_4) \rangle \langle F_{\alpha\beta}(t_2) F_{\alpha\beta}(t_3) \rangle .
 \end{aligned} \tag{142}$$

What is the physical significance of the decay (correlation) time τ ?

We interpret τ as the mean period of a lattice vibration since that would be the decay time for a fluctuating field generated by lattice vibrations.

This corresponds to a very short time and is our justification for assuming that no more than two times can fall within τ of each other. Since τ is the decay time for $f_{\alpha\beta}(t)$ we can make the following demands on $f_{\alpha\beta}(t)$ for $t \gg \tau$

$$\begin{aligned}
 & f_{\alpha\beta}(t) \simeq 0 \\
 \text{and} \quad & \int_t^\infty f_{\alpha\beta}(t') dt' \simeq 0 .
 \end{aligned} \tag{143}$$

Some functions that will arise in the ensuing formalism are

$$g_{\alpha\beta}(t) = \int_0^t f_{\alpha\beta}(t') dt' \tag{144}$$

and

$$h_{\alpha\beta}(t) = \int_0^t g_{\alpha\beta}(t') dt' . \tag{145}$$

In the case where $t \gg \tau$ we have by combining Equations (143), (144) and (145)

$$g_{\alpha\beta}(t) = g_{\alpha\beta}(\infty) = \gamma_{\alpha\beta} \tag{146}$$

and

$$h_{\alpha\beta}(t) = \gamma_{\alpha\beta} t , \tag{147}$$

where the constant $\gamma_{\alpha\beta}$ so defined will later be shown to have physical significance.

The last step in the construction of Sewell's model is to take the following results of previous theories⁽¹⁹⁾ as true:

$$\gamma_{\alpha\beta}, \Omega_{\alpha\beta} \ll \frac{1}{\tau}, \frac{kT}{\hbar} \quad , \quad (148)$$

$$\gamma_{\alpha\beta} \gg \Omega_{\alpha\beta} \quad \text{for } T > T_c \quad (149)$$

and $\gamma_{\alpha\beta} \ll \Omega_{\alpha\beta} \quad \text{for } T < T_c \quad , \quad (150)$

where T_c is a transition temperature on the order of one half the Debye temperature of the solid.

Application of the Sewell Model to a Simple Two-Site System

To get some feeling of how to handle the Sewell model we consider a very simple model consisting of a single polaron and two available sites. Since there are only two sites there is no necessity to retain the site subscripts α and β in this section.

Initially the polaron is localized at one of the two sites. We label this initial site 1. Our task is to find the transition probability for a transition to site 2. We can then look at the transition rate. To find the transition probability the time development operator will be used.

The part of the Hamiltonian governing the transitions is the interaction energy given by

$$H' = H_1 + H_2' = \frac{1}{2} \hbar \left(\Omega + F(t) \right) \left(c_1^* c_2 + c_2^* c_1 \right) \quad , \quad (151)$$

where we have used Equations (124) and (136). The differential equation for the time development operator is

$$i \hbar \frac{d}{dt} U(t) = H' U(t) \quad , \quad (152)$$

with initial condition

$$U(0) = 1 \quad . \quad (153)$$

From Equations (151) and (152) we can see that the solution is

$$U(t) = \exp \left\{ i \frac{\theta}{2} [c_1^* c_2 + c_2^* c_1] \right\} , \quad (154)$$

$$\text{where } \theta = \Omega t + \int_0^t F(t') dt' . \quad (155)$$

If we note that for a single particle state in a two site system

$$[c_1^* c_2 + c_2^* c_1]^2 = 1 \quad (156)$$

then it follows that

$$\begin{aligned} U(t) &= \cos \left[\frac{\theta}{2} (c_1^* c_2 + c_2^* c_1) \right] \\ &\quad + i \sin \left[\frac{\theta}{2} (c_1^* c_2 + c_2^* c_1) \right] \\ &= \cos \frac{\theta}{2} + i \sin \frac{\theta}{2} [c_1^* c_2 + c_2^* c_1] \end{aligned} \quad (157)$$

Since the initial condition was that the polaron was on site 1, its wave function at time zero is written

$$\psi(0) = c_1^* \mid 0 > . \quad (158)$$

At any time t later the wave function is

$$\psi(t) = U(t) \psi(0) . \quad (159)$$

Hence, from Equations (157) through (159) we have

$$\begin{aligned} \psi(t) &= \left\{ \cos \frac{\theta}{2} + i \sin \frac{\theta}{2} [c_1^* c_2 + c_2^* c_1] \right\} c_1^* \mid 0 > \\ &= \cos \frac{\theta}{2} c_1^* \mid 0 > + i \sin \frac{\theta}{2} c_2^* \mid 0 > . \end{aligned} \quad (160)$$

Thus, at time t the probability of finding the polaron at site 2 is

$$P_2(t) = \langle \sin^2 \frac{\theta}{2} \rangle . \quad (161)$$

If $\sin \theta/2$ is written in terms of the exponentials we have

$$\begin{aligned} P_2(t) &= \frac{1}{2} \langle \operatorname{Re} [1 - e^{i\theta}] \rangle \\ &= \frac{1}{2} \operatorname{Re} [1 - e^{i\Omega t} \langle \exp \left\{ i \int_0^t F(t') dt' \right\} \rangle] , \end{aligned} \quad (162)$$

where Re means take the real part. Note we have used Equation (155) in the last step of Equation (162).

We shall now derive an informative expression for $P_2(t)$ by rewriting the thermal average involved. Expanding the exponential yields

$$\begin{aligned} &\langle \exp \left\{ \int_0^t F(t') dt' \right\} \rangle \\ &= \langle 1 + i \int_0^t F(t') dt' \\ &\quad - \frac{1}{2!} \left\{ \int_0^t F(t') dt' \right\}^2 + \dots \rangle \\ &= 1 + i \int_0^t \langle F(t') \rangle dt' \\ &\quad - \frac{1}{2!} \int_0^t \int_0^t \langle F(t') F(t'') \rangle dt' dt'' \\ &\quad + \dots \end{aligned} \quad (163)$$

By Equations (137) and (139) every other term in Equation (163) vanishes so that Equation (163) becomes

$$\begin{aligned} &\langle \exp \left\{ i \int_0^t F(t') dt' \right\} \rangle \\ &= 1 - \frac{1}{2!} \int_0^t \int_0^t \langle F(t') F(t'') \rangle dt' dt'' + \dots \end{aligned} \quad (164)$$

Now Equations (138) and (140) can be used to simplify Equation (164) and write

$$\begin{aligned}
 & \langle \exp \left\{ i \int_0^t F(t') dt' \right\} \rangle \\
 &= 1 - \frac{1}{2} \left\{ \int_0^t \int_0^t f(|t' - t''|) dt' dt'' \right\} \\
 &+ \frac{3}{4!} \left\{ \int_0^t \int_0^t f(|t' - t''|) dt' dt'' \right\}^2 + \dots \\
 &= 1 - \left\{ \frac{1}{2} \int_0^t \int_0^t f(|t' - t''|) dt' dt'' \right\} + \frac{1}{2!} \left\{ \int_0^t \int_0^t f(|t' - t''|) dt' dt'' \right\} + \dots \\
 &= \exp \left\{ - \frac{1}{2} \int_0^t \int_0^t f(|t' - t''|) dt' dt'' \right\} . \tag{165}
 \end{aligned}$$

Equation (165) can be further simplified by noting that for $t \gg \tau$

$$\frac{1}{2} \int_0^t \int_0^t f(|t' - t''|) dt' dt'' = \gamma t . \tag{166}$$

This can be shown to be true because

$$\begin{aligned}
 & \frac{d}{dt} \left\{ \int_0^t \int_0^t f(|t' - t''|) dt' dt'' \right\} \\
 &= \frac{1}{2} \int_0^t f(|t' - t|) dt' + \frac{1}{2} \int_0^t f(|t - t''|) dt'' \\
 &= \int_0^t f(|t' - t|) dt' . \tag{167}
 \end{aligned}$$

Changing variables to $x = t' - t$ yields

$$\int_0^t f(|t' - t|) dt' = \int_{-t}^0 f(|x|) dx \tag{168}$$

but since f is an even function of x

$$+ \int_{-t}^0 f(|x|) dx = \int_0^t f(|x|) dx = g(t) \quad (169)$$

where we have also used Equation (144). For $t \gg \tau$ we can use Equation (146) and thus from Equations (167) through (169)

$$\frac{d}{dt} \left\{ \frac{1}{2} \int_0^t \int_0^t f(|t' - t''|) dt' dt'' \right\} = \gamma \quad (170)$$

and, hence, Equation (166) is valid. From Equations (165), (166) and (162) we have

$$P_2(t) = \frac{1}{2} [1 - \cos \Omega t e^{-\gamma t}] \quad (171)$$

for $t \gg \tau$.

If we retraced the path leading to Equation (171) we would see that the $\cos \Omega t$ originated in the tunneling interaction H_1 whereas the $e^{-\gamma t}$ arose solely from H_2' . Thus, in the absence of H_2' the polaron would oscillate with frequency Ω between sites 1 and 2.

We are particularly interested in high temperatures where $T > T_c$ so that $\Omega \ll \gamma$ and we can write

$$P_2(t) = \frac{1}{2} [1 - e^{-\gamma t}] \quad (172)$$

Noting that the probability of occupation of site 1 as a function of time is

$$P_1(t) = 1 - P_2(t) \quad , \quad (173)$$

we can calculate the time rate of change of P_2 as

$$\frac{dP_2}{dt} = \frac{\gamma}{2} e^{-\gamma t} = \frac{\gamma}{2} [P_1 - P_2] \quad (174)$$

Since P_2 changes either when site 2 is occupied and a jump occurs to site 1 or else when site 1 is occupied and a jump occurs to site 2 we can write a word equation

$$\begin{aligned}
 \frac{dP_2}{dt} &= \left(\begin{array}{c} \text{Time rate of change} \\ \text{of } P_2 \end{array} \right) \\
 &= \left(\begin{array}{c} \text{Probability that} \\ \text{site 1 is occupied} \end{array} \right) \left(\begin{array}{c} \text{Jump} \\ \text{frequency} \end{array} \right) \\
 &\quad - \left(\begin{array}{c} \text{Probability that} \\ \text{site 2 is occupied} \end{array} \right) \left(\begin{array}{c} \text{Jump} \\ \text{frequency} \end{array} \right) \\
 &= \left(\begin{array}{c} \text{Jump} \\ \text{frequency} \end{array} \right) (P_1 - P_2)
 \end{aligned} \tag{175}$$

Comparison of Equations (174) and (175) identifies $\frac{1}{2} \gamma$ as the jump frequency or transition rate.

Dielectric Properties of the Sewell Two Site Model

Consider now the application of an electric field

$$\vec{E}(t) = \vec{E}(\omega) e^{-i\omega t} \tag{176}$$

to the system. The direction of the electric field is chosen to lie along the direction from site 1 to site 2. This direction is labeled the $\hat{x}$ direction with $x = +a$ at site 1 and $x = -a$ at site 2. Then from Equation (135) it follows that

$$\vec{m} = -e_0 a (c_1^* c_1 - c_2^* c_2) \hat{x} \tag{177}$$

The externally applied electric field induces a dipole moment

$$\vec{m}(t) = K(\omega) E(\omega) e^{i\omega t}, \tag{178}$$

where $K(\omega)$ contains the dielectric properties since

$$\epsilon(\omega) = 1 + 4\pi K(\omega) \tag{179}$$

The response function $K(t)$ is the Fourier transform of $K(\omega)$ defined by

$$K(\omega) = \int_0^\infty K(t) e^{-i\omega t} dt. \tag{180}$$

The application of the electric field leads to an extra term in the Hamiltonian given by

$$H_3 = - \vec{m} \cdot \vec{E}(t) = - m E(t) \quad , \quad (181)$$

where $\vec{m}$ is the operator given in Equation (177). This extra term H_3 can be related to the response function $K(t)$ by the fluctuation-dissipation theorem of Kubo.⁽²⁷⁾ The expression given by Sewell⁽²²⁾ is

$$K(t) = - \frac{1}{2kT} < [\dot{m}(t) , m(0)]_+ >_{Av} \quad , \quad (182)$$

where $m(t)$ is the Heisenberg operator defined by

$$m(t) = U^\dagger(t) m U(t) \quad . \quad (183)$$

The commutator is evaluated in Appendix E. The brackets $< >_{Av}$ imply a thermal average taken over the system of the particle plus reservoir in the absence of an applied field.

Since H_1 and H_2' are weak perturbations we assume in first approximation that the particle and reservoir are uncoupled and write

$$< >_{Av} = << >_{ptcl} > \quad , \quad (184)$$

where $< >_{ptcl}$ means an average over all the single particle states and $< >$ is the thermal average over the reservoir introduced in Equation (137) in analogy with Equation (126). Thus, Equation (182) becomes

$$K(t) = - \frac{1}{4kT} \sum_{\alpha} << 0 \left| c_{\alpha} [\dot{m}(t) , m]_+ c_{\alpha}^* \right| 0 >> \quad . \quad (185)$$

From Equations (E2) and (185)

$$\begin{aligned} K(t) &= - \frac{e_o^2 a^2}{kT} < \frac{d}{dt} \cos \theta > \\ &= \frac{e_o^2 a^2}{kT} \frac{d}{dt} \text{Re} \left[\left\langle e^{i\theta} \right\rangle \right] \quad . \end{aligned} \quad (186)$$

Now $< e^{i\theta} >$ is something we have seen before, in fact, from Equations (162), (171) and (186) we can deduce for $t \gg \tau$

$$K(t) = - \frac{e_o^2 a^2}{kT} \frac{d}{dt} \left[\cos \Omega t e^{-\gamma t} \right] \quad . \quad (187)$$

To obtain the frequency dependence we combine Equations (180) and (187) to get

$$K(\omega) = - \frac{e_o^2 a^2}{kT} \int_0^\infty \frac{d}{dt} [\cos \Omega t e^{-\gamma t}] e^{-i\omega t} dt \quad (188)$$

Integrating by parts yields

$$K(\omega) = \left\{ \frac{e_o^2 a^2}{kT} \left[1 - \omega^2 \frac{\gamma^2 + \omega^2 - \Omega^2}{(\gamma^2 + \Omega^2 - \omega^2)^2 + 4\omega^2 \gamma^2} \right] \right\} - i \left\{ \frac{e_o^2 a^2}{kT} \omega \gamma \frac{\gamma^2 + \omega^2 + \Omega^2}{(\gamma^2 + \Omega^2 - \omega^2)^2 + 4\omega^2 \gamma^2} \right\} \quad (189)$$

Looking back at Equations (149) and (150) we see that the frequency response is quite different for $T < T_c$ than $T > T_c$. In particular, for $T < T_c$ we have

$$\text{Re } K(\omega) \simeq \frac{e_o^2 a^2}{kT} \left[1 - \frac{\omega^2}{\Omega^2 + \omega^2} \right] \quad (190)$$

so that there is a strong resonance near $\omega = \Omega$. For $T > T_c$, the imaginary part shows the behavior

$$\text{Im } K(\omega) \simeq - \frac{e_o^2 a^2}{kT} \frac{\omega \gamma}{\omega^2 + \gamma^2} \quad (191)$$

Now Equation (191) has a maximum at $\omega = \gamma$ and since dielectric losses are proportional to $\text{Im } K(\omega)$ one would expect the losses to peak near that frequency.

Thus, for the two site model we have a transition from resonance behavior to Debye loss behavior as the sample temperature passes through T_c . This sort of behavior has not yet been observed for a real material, although a tunneling to hopping behavior has been reported in the conductivity in glasses containing transition metal oxides.⁽²⁸⁾

Application of the Sewell Model to Conduction in the Periodic Lattice

Now consider the polaron in the periodic lattice upon application of the external field of Equation (176). Because of the periodicity of the lattice we are investigating the response of n polarons where n is small compared to the total number of unit cells. The small number density of polarons insures the validity of neglecting polaron-polaron interactions. We relate the current density $\vec{J}$ to the applied field via the conductivity tensor $\sigma_{\mu\nu}$, that is,

$$J_{\mu}(t) = \sigma_{\mu\nu}(\omega) E_{\nu}(\omega) e^{i\omega t} \quad (192)$$

The Fourier transform of the conductivity, $\sigma_{\mu\nu}(t)$, is defined by

$$\sigma_{\mu\nu}(\omega) = \int_0^{\infty} \sigma_{\mu\nu}(t) e^{-i\omega t} dt \quad (193)$$

From the fluctuation-dissipation theorem of Kubo⁽²⁷⁾ it follows that

$$\sigma_{\mu\nu}(t) = \frac{n_0}{2kT} \langle [\dot{m}_{\mu}(t), \dot{m}_{\nu}(0)]_+ \rangle_{Av} \quad (194)$$

where

$$n_0 = n/(\text{crystal volume}) \quad (195)$$

is the volume density of polarons. We again assume that in first approximation the polarons and reservoir are uncoupled so that Equation (184) is appropriate.

As in the two site model for any operator Q we have

$$\langle Q \rangle_{ptcl} = \frac{\sum_{\alpha} \langle 0 | c_{\alpha} Q c_{\alpha}^* | 0 \rangle}{\sum_{\alpha} \langle 0 | c_{\alpha} c_{\alpha}^* | 0 \rangle} \quad (196)$$

but in this N site model the denominator is N whereas in the two site model the denominator was 2. From Equations (184), (194), and (196) we have

$$\sigma_{\mu\nu}(t) = \frac{n_0}{NkT} \sum_{\alpha} \langle \langle 0 | c_{\alpha} \dot{m}_{\mu}(t) \dot{m}_{\nu}(0) c_{\alpha}^* | 0 \rangle \rangle, \quad (197)$$

where we have used the fact that $\dot{m}_{\mu}(t)$ commutes with $\dot{m}_{\nu}(0)$.

We consider a model such that all sites are equivalent so that we can do the sum on α by just multiplying the expression for any particular site

(say $\alpha = 0$) by N to get

$$\sigma_{\mu\nu}(t) = \frac{n_0}{kT} \ll 0 \left| c_0 \dot{m}_\mu(t) \dot{m}_\nu(0) c_0^* \right| 0 \gg . \quad (198)$$

To make further progress in Equation (198) it is convenient to insert the projection operator

$$\sum_\alpha c_\alpha^* \left| 0 \right\rangle \langle 0 \left| c_\alpha = 1 \quad (199)$$

to write

$$\sigma_{\mu\nu}(t) = \frac{n_0}{kT} \sum_\alpha \ll 0 \left| c_0 \dot{m}_\mu(t) c_\alpha^* \right| 0 \right\rangle \langle 0 \left| c_\alpha \dot{m}_\nu(0) c_0^* \right| 0 \gg \quad (200)$$

We now assume $T > T_c$; that is, assume the jumping process predominates so that Equation (152) becomes

$$i\hbar \frac{d}{dt} U(t) = H_2' U(t) , \quad (201)$$

so this with Equation (183) yields

$$i\hbar \frac{d\vec{m}(t)}{dt} = U^\dagger(t) \left[\vec{m} , H_2' \right] U(t) . \quad (202)$$

Now

$$U(t) = \exp \left\{ - i H_2' t \right\} \quad (203)$$

is the solution to Equation (201) so to lowest order in H_2'

$$i\hbar \frac{d\vec{m}(t)}{dt} = \left[\vec{m} , H_2' \right] . \quad (204)$$

Now we have the tools to attack Equation (200). Consider the term

$$\begin{aligned} i\hbar \langle 0 \left| c_0 \dot{\vec{m}}(t) c_\alpha^* \right| 0 \rangle \\ = \langle 0 \left| c_0 \left[\vec{m} , H_2' \right] c_\alpha^* \right| 0 \rangle \end{aligned} \quad (205)$$

by Equation (204). Writing the commutator explicitly and then inserting the projection operator of Equation (199) yields

$$\begin{aligned}
& \langle 0 \mid c_0 [\vec{m}, H_2'] c_\alpha^* \mid 0 \rangle \\
&= \sum_\beta \left\{ \langle 0 \mid c_0 \vec{m} c_\beta^* \mid 0 \rangle \langle 0 \mid c_\beta H_2' c_\alpha^* \mid 0 \rangle \right. \\
&\quad \left. - \langle 0 \mid c_0 H_2' c_\beta^* \mid 0 \rangle \langle 0 \mid c_\beta \vec{m} c_\alpha^* \mid 0 \rangle \right\}. \quad (206)
\end{aligned}$$

The expectation values involving $\vec{m}$ can be evaluated by applying Equation (135) to write, for example,

$$\begin{aligned}
\langle 0 \mid c_0 \vec{m} c_\beta^* \mid 0 \rangle &= -e_0 \langle 0 \mid c_0 \sum_\gamma \vec{a}_\gamma c_\gamma^* c_\gamma c_\beta^* \mid 0 \rangle \\
&= -e_0 \langle 0 \mid c_0 \vec{a}_\beta c_\beta^* \mid 0 \rangle = -e_0 \vec{a}_\beta \delta_{0\beta} = 0 \quad (207)
\end{aligned}$$

because $\vec{a}_0 = 0$ by our choice of origin. Similarly, we have

$$\langle 0 \mid c_\beta \vec{m} c_\alpha^* \mid 0 \rangle = -e_0 \vec{a}_\alpha \delta_{\alpha\beta}. \quad (208)$$

Hence, from Equations (205) through (208)

$$\begin{aligned}
i\hbar \langle 0 \mid c_0 \dot{\vec{m}}(t) c_\alpha^* \mid 0 \rangle \\
&= e_0 \sum_\beta \vec{a}_\alpha \delta_{\alpha\beta} \langle 0 \mid c_0 H_2' c_\beta^* \mid 0 \rangle \\
&= e_0 \vec{a}_\alpha \langle 0 \mid c_0 H_2' c_\alpha^* \mid 0 \rangle. \quad (209)
\end{aligned}$$

By Equation (136) we can substitute for H_2' in Equation (209) and obtain

$$i\hbar \langle 0 \mid c_0 \dot{\vec{m}}(t) c_\alpha^* \mid 0 \rangle = e_0 \vec{a}_\alpha \frac{\hbar}{2} F_{0\alpha}(t). \quad (210)$$

Evaluating the brackets appearing in Equation (200) by the result of Equation (210) yields

$$\langle 0 \mid c_0 \dot{\vec{m}}_\mu(t) c_\alpha^* \mid 0 \rangle = -\frac{i}{2} e_0 a_{\alpha\mu} F_{0\alpha}(t) \quad (211)$$

and

$$\langle 0 | c_{\alpha} \dot{m}_v(0) c_0^* | 0 \rangle = \frac{i}{2} e_0 a_{\alpha\mu} F_{0\alpha}(0) \quad (212)$$

The response function of Equation (200) is, therefore,

$$\begin{aligned} \sigma_{\mu\nu}(t) &= \frac{n_0 e_0^2}{4kT} \sum_{\alpha} \langle F_{0\alpha}(t) F_{0\alpha}(0) \rangle a_{\alpha\mu} a_{\alpha\nu} \\ &= \frac{n_0 e_0^2}{4kT} \sum_{\alpha} f_{0\alpha}(t) a_{\alpha\mu} a_{\alpha\nu} \quad (213) \end{aligned}$$

Thus, the frequency dependent conductivity tensor of Equation (193) becomes

$$\sigma_{\mu\nu}(\omega) = \frac{n_0 e_0^2}{4kT} \sum_{\alpha} a_{\alpha\mu} a_{\alpha\nu} \int_0^{\infty} f_{0\alpha}(t) e^{-i\omega t} dt \quad (214)$$

Now $f_{0\alpha}(t)$ decays in a time τ so for $\omega \ll 1/\tau$ (ω small compared to the reststrahl frequency) we can write

$$\int_0^{\infty} f_{0\alpha}(t) e^{-i\omega t} dt \simeq \int_0^{\infty} f_{0\alpha}(t) dt = \gamma_{0\alpha} \quad (215)$$

Finally combining Equations (214) and (215) we have

$$\sigma_{\mu\nu}(\omega) = \frac{n_0 e_0^2}{4kT} \sum_{\alpha} a_{\alpha\mu} a_{\alpha\nu} \gamma_{0\alpha} \quad (216)$$

Our two site model interpretation of γ was that it is twice the jump frequency. In the present case we expect $\gamma_{0\alpha}$ to be the jump frequency from site 0 to site α . We might write a simple minded expression for $\gamma_{0\alpha}$ as

$$\gamma_{0\alpha} = 2 \frac{\omega_0}{2\pi} e^{-E_{0\alpha}/kT} \quad (217)$$

Further, we expect $\gamma_{0\alpha}$ to be smaller the farther α is from 0 so that if we only counted nearest neighbors the diagonal conductivity element would be

$$\sigma = \frac{n_0 e^2}{2kT} N_{nn} \frac{\omega_0}{2\pi} e^{-E_0/kT} \quad (218)$$

where N_{nn} is the number of nearest neighbors and E_0 is the activation energy needed to jump from site 0 to any of its equivalent nearest neighbors. The mobility corresponding to Equation (218) is

$$\mu = \frac{e_0}{2kT} N_{nn} \frac{\omega_0}{2\pi} e^{-E_0/kT} \quad (219)$$

Holstein⁽¹⁹⁾ obtains a similar expression in his one dimensional model obtaining

$$\mu = \frac{e_0}{kT} a^2 \frac{\omega_0}{2\pi} e^{-E_a/kT} \quad (220)$$

in the high T limit where E_a is an activation energy. The $1/T$ dependence of the pre-factor in Equations (219) and (220) is a result of the particular model. For example, a different model⁽²⁵⁾ yields in the high T limit

$$\mu = \frac{e_0}{kT} a^2 \frac{I^2}{2\hbar} \sqrt{\pi/kTE^*} e^{-E^*/kT}, \quad (221)$$

where E^* is an activation energy and I is a nearest neighbor exchange integral. Note in Equation (221) the temperature dependence of the pre-factor goes as $1/T^{3/2}$.

Other Small Polaron Work

We have just introduced small polaron theory. The work of Holstein has been continued⁽²⁹⁾ and the Hall effect has been investigated in the region where the hopping motion predominates. There it is shown that upon application of an external magnetic field the existence of the Hall effect involves the occupation of at least three lattice sites. It is shown that for an electron originally on one of these sites the relative transition probability to either of the two remaining sites involves a term linear in the vector field. Some Hall effect calculations also appear in the paper by Kurosawa.⁽³⁰⁾

The optical properties of ionic crystals have also been investigated in the small polaron region. Eagles⁽³¹⁾ employs a small polaron approach to calculate the optical absorption assuming that the index of refraction is known.

ACKNOWLEDGEMENTS

I am grateful to Dr. Gary J. Dau and Dr. R. L. Gordon for the hospitality extended to me during my summer at the Battelle-Northwest facilities. I would especially like to express my appreciation to Dr. S. C. Keeton, Dr. R. R. Bourassa, and Mr. Barry Green for many stimulating discussions. The excellent effort given to preparing this manuscript by Mrs. Linda Tipton is gratefully acknowledged.

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APPENDICES

We shall employ Equation (13) to evaluate the parameter μ introduced in Equation (2). To evaluate μ consider a static situation so that

$$\vec{P}(\vec{r}) = 0 \quad (A1)$$

and, consequently, Equation (13) becomes

$$\vec{P}(\vec{r}) = \frac{1}{2\mu\omega} \vec{D}(\vec{r}) \quad (A2)$$

The procedure now is to derive a second equation relating $\vec{P}(\vec{r})$ to $\vec{D}(\vec{r})$ in the static case, and hence to obtain an expression for μ .

In the static case we can write

$$\vec{D} = \epsilon_s \vec{E} = \vec{E} + 4\pi \vec{P}_{\text{total}} \quad (A3)$$

where ϵ_s is the static dielectric constant. $\vec{P}_{\text{total}}$, the total static polarization, can be written as the sum of two parts, one due to the lattice polarization and the other due to the electronic polarization: i.e.,

$$\vec{P}_{\text{total}} = \vec{P} + \vec{P}_{\text{elec}} \quad (A4)$$

Note that the unsubscripted $\vec{P}$ is the same as $\vec{P}(\vec{r})$; it is the lattice polarization. From Equation (A3) we have

$$\vec{P}_{\text{total}} = \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_s} \right) \vec{D} \quad (A5)$$

Hence, from Equations (A4) and (A5) we have

$$\vec{P} = \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_s} \right) \vec{D} - \vec{P}_{\text{elec}} \quad (A6)$$

To replace $\vec{P}_{\text{elec}}$ in Equation (A6) think of going to frequencies too high for the lattice to respond yet low enough so that the electrons can still respond. In this limit

$$\begin{aligned} \vec{P}_{\text{total}} &\longrightarrow \vec{P}_{\text{elec}} \\ \epsilon_s &\longrightarrow \epsilon_\infty \end{aligned} \quad (A7)$$

and an equation analogous to Equation (A5) can be written,

$$\vec{P}_{\text{elec}} = \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_{\infty}} \right) \vec{D} \quad (\text{A8})$$

Combining Equations (A6) and (A8) yields

$$\vec{P}(\vec{r}) = \frac{1}{4\pi} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_S} \right) \vec{D}(\vec{r}) \quad (\text{A9})$$

It is usual to define an average dielectric constant by

$$\bar{\epsilon} = \frac{\epsilon_{\infty} \epsilon_S}{\epsilon_S - \epsilon_{\infty}} \quad (\text{A10})$$

so that Equation (A9) becomes

$$\vec{P}(\vec{r}) = \frac{1}{4\pi\bar{\epsilon}} \vec{D}(\vec{r}) \quad (\text{A11})$$

Comparison of Equations (A2) and (A11) yields Equation (3) for μ .

To arrive at Equation (111) we consider the Hamiltonian of an electron in a rigid lattice which we write as

$$H_{el}^0 = \frac{p^2}{2m} + U_0 + \sum_i V_i \quad (B1)$$

where the first term is obviously the kinetic energy, U_0 is the interaction between the electron and the positive ion at its site, and $\sum_i V_i$ is the interaction of the electron with all the other rigid ions.

Our model is a localized electron model which assumes localized states Ψ_α which satisfy

$$\left(\frac{p^2}{2m} + U_0 \right) \Psi_\alpha = \epsilon_\alpha^0 \Psi_\alpha \quad (B2)$$

with

$$\langle \Psi_\alpha | \Psi_\beta \rangle = \delta_{\alpha\beta} \quad (B3)$$

To transform H_{el}^0 to quantized form we compute

$$\begin{aligned} H_{el} &= \langle \sum_\alpha c_\alpha \Psi_\alpha | H_{el}^0 | \sum_\beta c_\beta \Psi_\beta \rangle \\ &= \sum_\alpha c_\alpha^* c_\alpha \epsilon_\alpha^0 + \sum_{\alpha, \beta} c_\alpha^* c_\beta \langle \Psi_\alpha | \sum_i V_i | \Psi_\beta \rangle \end{aligned} \quad (B4)$$

where we have used Equations (B1) through (B3). Putting all the local terms together by defining

$$\epsilon_\alpha = \epsilon_\alpha^0 + \langle \Psi_\alpha | \sum_i V_i | \Psi_\alpha \rangle \quad (B5)$$

we obtain

$$H_{el} = \sum_\alpha \epsilon_\alpha c_\alpha^* c_\alpha + \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} c_\alpha^* c_\beta J_{\alpha\beta} \quad (B6)$$

where

$$J_{\alpha\beta} = \langle \Psi_\alpha | \sum_i V_i | \Psi_\beta \rangle \quad (B7)$$

Equation (B6) is identical to Equation (111).

APPENDIX C

We wish in this Appendix to derive Equation (118). From Equations (110) through (116) we have

$$\begin{aligned}
 H = & e^{-B} \left(\sum_{\alpha} \epsilon_{\alpha} c_{\alpha}^* c_{\alpha} \right) e^B + e^{-B} \left(\sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} c_{\alpha}^* c_{\beta} J_{\alpha\beta} \right) e^B \\
 & + e^{-B} \left(\sum_{\lambda} \frac{1}{2} \left[p_{\lambda}^2 + \omega_{\lambda}^2 q_{\lambda}^2 \right] \right) e^B + e^{-B} \left(\sum_{\alpha, \lambda} k_{\alpha\lambda} c_{\alpha}^* c_{\alpha} q_{\lambda} \right) e^B \\
 & + e^{-B} \left(\sum_{\substack{\alpha, \beta, \lambda \\ \alpha \neq \beta}} L_{\alpha\beta\lambda} c_{\alpha}^* c_{\beta} q_{\lambda} \right) e^B . \quad (C1)
 \end{aligned}$$

We shall compute the transformation term by term. Our first term is to be calculated using the algebraic identity of Equation (83) so that also using the definition of B from Equation (117) we have

$$e^{-B} \left(\sum_{\alpha} c_{\alpha}^* c_{\alpha} \epsilon_{\alpha} \right) e^B = \sum_{\alpha} \epsilon_{\alpha} c_{\alpha}^* c_{\alpha} , \quad (C2)$$

where the virtue of Equation (83) again appears when one of its early commutators vanishes, which in this case is

$$\left[\sum_{\alpha} \epsilon_{\alpha} c_{\alpha}^* c_{\alpha} , \sum_{\beta} c_{\beta}^* c_{\beta} \frac{K_{\beta\lambda}}{\omega_{\lambda}} \frac{i}{\hbar} p_{\lambda} \right] = 0 . \quad (C3)$$

The next piece to calculate is $e^{-B} \left[\sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} c_{\alpha}^* c_{\beta} \right] e^B$.

In this calculation we must use the anti-commutation properties of the fermion operators

$$\begin{aligned}
 [c_{\alpha} , c_{\beta}^*]_{+} &= \delta_{\alpha\beta} \\
 [c_{\alpha} , c_{\beta}]_{+} &= [c_{\alpha}^* , c_{\beta}^*]_{+} = 0 . \quad (C4)
 \end{aligned}$$

Expanding the exponentials and employing the explicit form of B (Equation (117)) yields

$$\begin{aligned}
& e^{-B} \left[\sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} J_{\alpha\beta} c_{\alpha}^* c_{\beta} \right] e^B \\
&= \left(1 - \sum_{\gamma, \lambda} c_{\gamma}^* c_{\gamma} \frac{K_{\gamma\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} + \dots \right) \sum_{\alpha, \beta} J_{\alpha\beta} c_{\alpha}^* c_{\beta} \left(1 + \sum_{\gamma, \lambda} c_{\gamma}^* c_{\gamma} \frac{K_{\gamma\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} + \dots \right) \\
&= \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \left[c_{\alpha}^* - \sum_{\gamma, \lambda} c_{\gamma}^* c_{\gamma} c_{\alpha}^* \frac{K_{\gamma\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} + \dots \right] J_{\alpha\beta} \left[c_{\beta} + \sum_{\gamma, \lambda} c_{\beta} c_{\gamma}^* c_{\gamma} \frac{K_{\gamma\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} + \dots \right] \\
&= \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \left(c_{\alpha}^* - \sum_{\lambda} c_{\alpha}^* \frac{K_{\alpha\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} + \dots \right) J_{\alpha\beta} \left(c_{\beta} + \sum_{\lambda} c_{\beta} \frac{K_{\beta\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} + \dots \right) \\
&= \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \exp \left\{ - \sum_{\lambda} \frac{K_{\alpha\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} \right\} J_{\alpha\beta} c_{\alpha}^* c_{\beta} \exp \left\{ \sum_{\lambda} \frac{K_{\beta\lambda}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\lambda} \right\} . \quad (C5)
\end{aligned}$$

Note that we used the fact that any state under consideration is a single electron state so that two destruction operators in a row operating on the state yield a zero result and hence such products have not been allowed in Equation (C5).

The third piece of H to calculate is obtained by again appealing to the identity Equation (83) so that

$$\begin{aligned}
e^{-B} H_{ph} e^B &= H_{ph} + [H_{ph}, B] + \frac{1}{2!} [[H_{ph}, B], B] + \dots \\
&= H_{ph} + \left[\sum_{\lambda} \frac{1}{2} \omega_{\lambda}^2 Q_{\lambda}, \sum_{\alpha, \gamma} c_{\alpha}^* c_{\alpha} \frac{K_{\alpha\gamma}}{\omega_{\lambda}} \frac{i}{2\hbar} p_{\gamma} \right] + \dots \\
&= H_{ph} + \frac{1}{2} \sum_{\alpha, \gamma, \lambda} \omega_{\lambda}^2 c_{\alpha}^* c_{\alpha} \frac{K_{\alpha\gamma}}{\omega_{\lambda}} [Q_{\lambda}^2, \frac{i}{2\hbar} p_{\gamma}] + \dots \\
&= H_{ph} - \sum_{\alpha, \lambda} c_{\alpha}^* c_{\alpha} K_{\alpha\lambda} Q_{\lambda} + \dots
\end{aligned}$$

APPENDIX D

We here wish to calculate the integral $\langle \psi_\alpha(\vec{x}) | \vec{x} | \psi_\beta(\vec{x}) \rangle$ assuming that the wave functions are s states. This assumption implies that $\psi_\alpha(\vec{x})$, for example, is invariant under the transformation

$$(\vec{x} - \vec{a}_\alpha) \longrightarrow (\vec{a}_\alpha - \vec{x}) \quad (D1)$$

where $\vec{a}_\alpha$ is the position of the parent ion. Analogously, $\psi_\beta(\vec{x})$ is invariant under the transformation

$$(\vec{x} - \vec{a}_\beta) \longrightarrow (\vec{a}_\beta - \vec{x}) \quad (D2)$$

Our first step in the calculation is to show that $\psi_\beta(\vec{x})$ is invariant under Expression (D1):

$$\begin{aligned} \psi_\beta(\vec{x} - \vec{a}_\alpha) &= \psi_\beta \left\{ (\vec{x} - \vec{a}_\alpha + \vec{a}_\beta) - \vec{a}_\beta \right\} \\ &= \psi_\beta \left\{ -(\vec{x} - \vec{a}_\alpha + \vec{a}_\beta) + \vec{a}_\beta \right\} = \psi_\beta(\vec{a}_\alpha - \vec{x}) \end{aligned} \quad (D3)$$

where we employed Expression (D2) for $\vec{x}$ replaced by $(\vec{x} - \vec{a}_\alpha + \vec{a}_\beta)$.

Now we calculate the integral by writing

$$\begin{aligned} \langle \psi_\alpha(\vec{x}) | \vec{x} | \psi_\beta(\vec{x}) \rangle \\ = \langle \psi_\alpha(\vec{x}) | \vec{a}_\alpha | \psi_\beta(\vec{x}) \rangle + \langle \psi_\alpha(\vec{x}) | (\vec{x} - \vec{a}_\alpha) | \psi_\beta(\vec{x}) \rangle \end{aligned} \quad (D4)$$

Now we manipulate the second term on the right hand side of Equation (D4) by writing

$$\begin{aligned} \langle \psi_\alpha(\vec{x}) | (\vec{x} - \vec{a}_\alpha) | \psi_\beta(\vec{x}) \rangle \\ = \langle \psi_\alpha(\vec{x} - \vec{a}_\alpha) | (\vec{x} - \vec{a}_\alpha) | \psi_\beta(\vec{x} - \vec{a}_\alpha) \rangle \\ = - \langle \psi_\alpha(\vec{x} - \vec{a}_\alpha) | (\vec{x} - \vec{a}_\alpha) | \psi_\beta(\vec{x} - \vec{a}_\alpha) \rangle = 0 \end{aligned} \quad (D5)$$

where we have used the invariance of ψ_α and ψ_β under the transformation of Expression (D1). From Equations (D4) and (D5) it follows that

$$\langle \psi_\alpha | \vec{x} | \psi_\beta \rangle = \delta_{\alpha\beta} \vec{a}_\alpha \quad (D6)$$

APPENDIX E

To calculate the anti-commutator of Equation (182) we must first calculate $m(t)$ as given in Equation (183). From Equations (157) and (183) we have

$$\begin{aligned}
 m(t) &= \left\{ \cos \frac{\theta}{2} - i \left(c_2^* c_1 + c_1^* c_2 \right) \sin \frac{\theta}{2} \right\} \left\{ -e_0 a \left(c_1^* c_1 - c_2^* c_2 \right) \right\} \\
 &\quad \cdot \left\{ \cos \frac{\theta}{2} + i \left(c_2^* c_1 + c_1^* c_2 \right) \sin \frac{\theta}{2} \right\} \\
 &= -e_0 a \left\{ \cos^2 \frac{\theta}{2} \left(c_1^* c_1 - c_2^* c_2 \right) \right. \\
 &\quad + \sin^2 \frac{\theta}{2} \left(c_2^* c_1 + c_1^* c_2 \right) \left(c_1^* c_1 - c_2^* c_2 \right) \left(c_2^* c_1 + c_1^* c_2 \right) \\
 &\quad - i \sin \frac{\theta}{2} \cos \frac{\theta}{2} \left(c_2^* c_1 + c_1^* c_2 \right) \left(c_1^* c_1 - c_2^* c_2 \right) \\
 &\quad \left. + i \sin \frac{\theta}{2} \cos \frac{\theta}{2} \left(c_1^* c_1 - c_2^* c_2 \right) \left(c_2^* c_1 + c_1^* c_2 \right) \right\} \\
 &= -e_0 a \left\{ \cos^2 \frac{\theta}{2} \left(c_1^* c_1 - c_2^* c_2 \right) - \sin^2 \frac{\theta}{2} \left(c_1^* c_1 - c_2^* c_2 \right) \right. \\
 &\quad \left. + i \sin \frac{\theta}{2} \cos \frac{\theta}{2} \left(c_1^* c_2 - c_2^* c_1 \right) \right\} \\
 &= -e_0 a \left\{ \cos \theta \left(c_1^* c_1 - c_2^* c_2 \right) + \frac{i}{2} \sin \theta \left(c_1^* c_2 - c_2^* c_1 \right) \right\}, \quad (E1)
 \end{aligned}$$

where we have, of course, used the fermion anti-commutation rules of Equation (C4).

From Equation (E1) it follows that

$$\begin{aligned}
 \left[\dot{m}(t), m \right]_+ &= \frac{d}{dt} \left[m(t), m \right]_+ \\
 &= \frac{d}{dt} e_0^2 a^2 \cos \theta \left[\left(c_1^* c_1 - c_2^* c_2 \right), \left(c_1^* c_1 - c_2^* c_2 \right) \right]_+ \\
 &= \frac{d}{dt} \left\{ 2 e_0^2 a^2 \cos \theta \left(c_1^* c_1 - c_2^* c_2 \right)^2 \right\} \\
 &= 2 e_0^2 a^2 \frac{d}{dt} (\cos \theta) \quad (E2)
 \end{aligned}$$

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