Self-Energy of the Polaron for Intermediate Temperatures*

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Approximate eigenvalues of the Fröhlich Hamiltonian, used as a model to represent the behavior of the electron coupled to the optical modes of an ionic crystal, are obtained for temperatures at which there is an appreciable probability of real phonons being present in the field. The method used is an extension of the variational technique employed by Gurari to obtain the eigenvalues at absolute zero. Correlations between phonons are neglected. The results obtained indicate that an electron in equilibrium with the lattice will have a strongly temperature-dependent effective mass for intermediate temperatures.

I. INTRODUCTION

THE approximate Hamiltonian derived by Fröhlich[1] to represent the behavior of the strongly interacting electrons and lattice oscillations in an ionic crystal is

$$H = H_0 + H_1, \tag{1}$$

$$H_0 = \frac{p^2}{2m} + \hbar\omega \sum_q a_q^\dagger a_q, \tag{2}$$

$$H_1 = 4\pi i \left(\frac{e^2 \hbar}{\gamma \omega V}\right)^{\frac{1}{2}} \sum_q \frac{1}{q}(a_q^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} - a_q e^{i\mathbf{q}\cdot\mathbf{r}}). \tag{3}$$

In the above expressions, p and r refer to the electron coordinates; ω is the characteristic optical phonon frequency and is obtained from the reststrahl frequency; $a_q^\dagger$ and a_q are creation and annihilation operators for phonons of wave vector q; V is the normalization volume; and γ is given by

$$\frac{1}{\gamma} = \frac{\omega^2}{4\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right), \tag{4}$$

where ϵ_∞ is the optical and ϵ_0 the static dielectric constant of the ionic crystal under consideration.

A number of approximations are made by Fröhlich in obtaining Eqs. (2) and (3). They are still valid at the higher temperatures presently under consideration.

Consider a polaron (the electron with its associated cloud of virtual phonons) in equilibrium with the lattice. At absolute zero, there is a vacuum of real phonons. The effect of finite temperatures is to put real phonons into the field, in addition to the virtual phonons surrounding the electron. If the temperature is not too high, it is reasonable to assume that these real phonons are described by the Bose distribution. Since the frequency is assumed to be independent of the wave vector, all modes of the system are equally excited.

The average number of phonons in each mode is given by

$$n = [e^{\Omega/T} - 1]^{-1}, \tag{5}$$

where Ω is defined by the relation $\hbar\omega = k\Omega$, and is of the order of magnitude of the Debye temperature.

A typical ionic crystal, NaCl, has $\Omega = 368°$ and $\Theta = 315°$. The values of n for two temperatures are

$T(°K)$	273	530
n	0.35	1.0

The validity of the present analysis is restricted to temperatures of the order of room temperature or lower.

II. CALCULATIONS

Following Fröhlich,[1] the Hamiltonian is most conveniently expressed in units of $\hbar\omega$, by defining the inverse length

$$u = (2m\omega/\hbar)^{\frac{1}{2}}, \tag{6}$$

and the dimensionless coupling constant

$$\alpha = \frac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{e^2 u}{\hbar\omega}. \tag{7}$$

For NaCl, the coupling constant is $\alpha \cong 5.5$.

The electron operators may be eliminated by applying the unitary transformation[2]

$$S = \exp(-i\sum a_{q'}^\dagger a_{q'} \mathbf{q'}\cdot\mathbf{r'}). \tag{8}$$

The resulting Hamiltonian is

$$H' = H_0' + H_1', \tag{1a}$$

$$H_0' = (\mathbf{K} - \sum_{q'} \mathbf{q'} a_{q'}^\dagger a_{q'})^2 + \sum_{q'} a_{q'}^\dagger a_{q'}, \tag{2a}$$

$$H_1' = i\left(\frac{4\pi\alpha}{V'}\right)^{\frac{1}{2}} \sum_{q'} \frac{1}{q'}(a_{q'}^\dagger - a_{q'}). \tag{3a}$$

V' and q' are now dimensionless quantities; V and q, introduced previously, were not. The dimensionless number K is a c number representing the total wave vector of the system; $(\mathbf{K} - \sum \mathbf{q'} a_{q'}^\dagger a_{q'})$ is clearly the electron wave vector.

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[1] H. Frölich, Advances in Phys. 3, 325 (1954). This review article contains references to earlier work in the field.

[2] Lee, Low, and Pines, Phys. Rev. 90, 297 (1953).

The calculations are performed by using the expression,

$$E = (\Psi, H\Psi); \quad (\Psi, \Psi) = 1, \tag{9}$$

which is stationary in the energy and has been employed previously to obtain eigenvalues at absolute zero.

The normalized wave function for the uncoupled fields in the (n, k) representation is[3]

$$\varphi_q = V'^{-\frac{1}{2}} \prod_{q'} |n_{q'}\rangle = V'^{-\frac{1}{2}} \prod_{q'} |n\rangle. \tag{10}$$

The physical model to be used as the basis of the trial wave function (valid in the intermediate coupling region with which we are concerned) is that the electron can be associated with an arbitrary number of virtual phonons in addition to the real phonons present. Correlations between phonons are neglected. However, some average effect of correlation is taken into account through the variational procedure. If one allows no more than unit changes in occupation number, the trial wave functions take on a rather simple form. Since the occupation number is at most of order unity for the temperatures of present interest, such trial functions take into reasonable account the various degenerate states of the uncoupled system which exist for these higher energies. The specific form of the normalized trial wave functions is postulated to be

$$\Psi_n = U\varphi_n; \quad U = \prod_{q'} U_{q'},$$

$$U_{q'} = [1 + V'^{-1}(|f_{q'}|^2 + |g_{q'}|^2)]^{-\frac{1}{2}} \tag{11}$$

$$\times [1 + V'^{-\frac{1}{2}}(f_{q'} a_{q'}{}^\dagger + g_{q'} a_{q'})].$$

Ψ_n is a generalization to higher temperatures of the trial functions used by Gurari for absolute zero.[4] The functions, f, f^*, g, and g^* are assumed to be unknown, independently varying functions of q' and K. The virtual phonon cloud surrounding the electron, as represented by the above trial function, is a semiclassical one, insofar that the field operators commute and the field components are independent of each other.[5]

Substitution of Eq. (11) in expression (9) yields, for large V',

$$E_n = E_n{}^0 + E_n{}^1, \tag{12}$$

where

$$E_n{}^0 = (\mathbf{K} - \sum_{q'} n\mathbf{q}')^2 + \sum_{q'} n, \tag{13}$$

[3] The n's in Eq. (10) are integers. The average values of n, obtained from Eq. (5), are substituted in the final result only.

[4] M. Gurari, Phil. Mag. 44, 329 (1954).

[5] The operator U does not represent a canonical transformation, since it is not unitary. Correction terms to the self-energy therefore cannot be calculated by the technique of reference 2. For a phonon vacuum, U is equivalent to (but not identical with) the unitary transformation $\bar{U}$, employed in reference 2.

and

$$E_n{}^1 = \{\mathbf{K} - V'^{-1} \sum_{q'} \mathbf{q}'[(n+1)|f_{q'}|^2 - n|g_{q'}|^2]\}^2$$
$$- K^2 + V'^{-1} \sum_{q'} \{(1+q'^2)(n+1)|f_{q'}|^2$$
$$- (1-q'^2)n|g_{q'}|^2 + i(4\pi\alpha)^{\frac{1}{2}}q'^{-1}$$
$$\times [(n+1)(f_{q'}{}^* - f_{q'}) - n(g_{q'}{}^* - g_{q'})]\}. \tag{14}$$

$E_n{}^0$ is the energy of the uncoupled field. The wave vector of the electron is equal to the total wave vector,

$$\mathbf{k}_{el} = (\mathbf{K} - \sum_{q'} n\mathbf{q}') = \mathbf{K}, \tag{15}$$

since $\sum_{q'} \mathbf{q}' = 0$. The energy of the uncoupled fields is therefore

$$E_n{}^0 = k^2 + nN, \tag{15a}$$

where N is the total number of optical phonon modes.

We minimize (12) by setting

$$\frac{\delta E_n}{\delta f} = \frac{\delta E_n}{\delta f^*} = \frac{\delta E_n}{\delta g} = \frac{\delta E_n}{\delta g^*} = 0. \tag{16}$$

Equation (16) serves to determine all the hitherto unknown functions. If we define κ_n to be[6]

$$\kappa_n = V'^{-1} \sum_{q'} \mathbf{q}'\{(n+1)|f_{q'}|^2 - n|g_{q'}|^2\}, \tag{17}$$

we obtain for f and g

$$f_{q'} = -(4\pi\alpha)^{\frac{1}{2}} i q'^{-1} [1 + q'^2 - 2\mathbf{q}' \cdot (\mathbf{K} - \kappa_n)]^{-1}, \tag{18}$$

and

$$g_{q'} = (4\pi\alpha)^{\frac{1}{2}} i q'^{-1} [-1 + q'^2 + 2\mathbf{q}' \cdot (\mathbf{K} - \kappa_n)]^{-1}. \tag{19}$$

The functions f^* and g^* are complex conjugates of f and g respectively.

Substitution of the explicit forms of f and g into expression (14) and rearrangement yields

$$E_n{}^1 = -\kappa_n{}^2 - \frac{4\pi\alpha}{V'} \sum_{q'} \frac{1}{q'^2} \left\{ \frac{n+1}{1 + q'^2 - 2\mathbf{q}' \cdot (\mathbf{K} - \kappa_n)} \right.$$
$$\left. + \frac{n}{-1 + q'^2 + 2\mathbf{q}' \cdot (\mathbf{K} - \kappa_n)} \right\}. \tag{20}$$

To complete the calculation, we allow the box normalization to go over into a continuum, replacing the sum by an integral and V' by $(2\pi)^3$. Two types of terms appear in Eq. (20): the term proportional to $(n+1)$ corresponds to phonon emission processes, and the term proportional to n to absorption processes. In the momentum region $K < 1$ (which is also the region where $|\mathbf{K} - \kappa_n| < 1$, as will be seen below), only virtual emissions and reabsorptions can take place. However, real absorptions and re-emissions can occur. Since we are interested only in virtual processes in the calculation of the self-energy, we must follow the usual method of taking principal values about the singularities to eliminate the real processes.

[6] Since $\mathbf{K}$ is the only direction present in the problem, κ_n must be a vector in the $\mathbf{K}$ direction.

The results of integration are

$$E_n^1 = -\kappa_n^2 - (n+1)\alpha \frac{\sin^{-1}(K-\kappa_n)}{K-\kappa_n},$$

and

$$\kappa_n = -\tfrac{1}{2}(n+1)\alpha \left\{ \frac{\sin^{-1}(K-\kappa_n)}{(K-\kappa_n)^2} \right.$$

$$\left. - \frac{1}{(K-\kappa_n)[1-(K-\kappa_n)^2]^{\frac{1}{2}}} \right\}. \quad (21)$$

An expansion in powers of k yields

$$E_n^1 = -\kappa_n^2 - (n+1)\alpha[1+\tfrac{1}{6}(K-\kappa_n)^2 + \cdots],$$

$$\kappa_n = K\left[\frac{\tfrac{1}{6}(n+1)\alpha}{1+\tfrac{1}{6}(n+1)\alpha} + O(K^2) \right]. \quad (22)$$

III. RESULTS AND DISCUSSION

Equation (22) can be used to obtain the results. In appropriate dimensions, they are, for $p^2/2m < \hbar\omega$,

$$\mathcal{E}_n = \hbar\omega E_n = E_{\text{osc}}^0 - (n+1)\alpha\hbar\omega + p^2/2m^* - O(p^4), \quad (23)$$

where

$$E_{\text{osc}}^0 = \hbar\omega nN, \quad (24)$$

and

$$m^* = m\{1 + \tfrac{1}{6}(n+1)\alpha\}. \quad (25)$$

The energy of the electron-phonon system therefore consists of three parts: the energy of the free phonon field; a lowering of the bottom of the conduction band; and an increase in the effective mass of the electron. All of these effects depend on n, and therefore on the temperature. At absolute zero, the results reduce to those obtained in references 2 and 3. For α small, they reduce to the results obtained from second order pertubation theory. But since in the actual physical situations $\tfrac{1}{6}\alpha \sim 1$, both the bottom of the band and the polaron mass are predicted to be rather strongly temperature-dependent in the present case.[7] This suggests that temperature-dependent terms, such as the effective mass, which are associated with the large magnitude of the electron-phonon coupling, should also appear in transport phenomena, for example, mobility measurements. Low and Pines[8] have calculated such intermediate-coupling effects in the vicinity of absolute zero.

One may object to the use of the variational procedure in the present case. The Ritz-Rayleigh procedure is most useful in obtaining upper limit estimates of the energy change of the ground state; that is, the band shift at absolute zero. To obtain good approximations to higher eigenvalues, we would need to use exact eigenfunctions for all previous eigenvalues, or else, to employ the Courant minimax principle. The situation is more serious with the effective-mass result than with the band shift, since the former represents the curvature, and therefore the second derivative of the curve of E versus k for an eigenvalue which in itself is not too well known.[9] The above results must therefore be taken only semiquantitatively. In their defense, one can say that the trial functions used represent a reasonable approximation to the physical situation and are essentially orthonormal. Further, since they are used in a stationary expression, the energy levels should not be too sensitive to errors in the trial function.

[7] A temperature dependence of effective mass and of band gap is also obtained in the case of electrons interacting with acoustical phonons. The effective coupling constant is of the order 10^{-5} smaller for this case than for the case of optical phonons in ionic crystals, so that this temperature dependence is negligibly small.

[8] F. E. Low and D. Pines, Phys. Rev. 98, 414 (1955).

[9] This difficulty already exists in the work of Lee, Low, and Pines. Their estimate of correction terms indicates that the error of their effective-mass results is more than four times as great as the error in the calculation of band shifts at absolute zero.