Weak-Coupling Theory of the Polaron Energy-Momentum Relation

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We present arguments to show that the energy-momentum relation for a polaron is quadratic for small k, but bends over and becomes horizontal when the energy approaches the optical-phonon energy above the ground state. We present a calculation for zero temperature based on a thermodynamic Green's-function theory which is especially designed to give a reliable polaron energy-momentum relation.

I. INTRODUCTION

IN 1950, Fröhlich *et al.*[1] introduced the notion that the interaction of an electron and the longitudinal optical mode of an ionic crystal could be treated like a particle-field interaction in much the same way as was the electron-phonon interaction in metals. Starting with the classical equations of motion of the polarization field, they derived a quantized Hamiltonian for the electron interacting with one mode of lattice vibration which was assumed to have a frequency ω independent of wave vector $\mathbf{q}$. The Hamiltonian is

$$H=-\nabla_r^2+\sum_q a_q^\dagger a_q+i(4\pi\alpha/V)^{1/2} \times\sum_q (1/q)(a_{-q}^\dagger-a_q)e^{i\mathbf{q}\cdot\mathbf{r}}, \quad (1)$$

where $a_q^\dagger$ and a_q create and annihilate a phonon with wave vector $\mathbf{q}$. We have taken $\hbar\omega$ and $(\hbar/2m\omega)^{1/2}$ to be the units of energy and length, respectively. The dimensionless coupling constant is

$$\alpha=e^2(m/2\omega\hbar^3)^{1/2}((1/\epsilon_\infty)-(1/\epsilon_0)).$$

The electron position and mass are r and m; the sample volume is V; the static and high-frequency dielectric constants are ϵ_0 and ϵ_∞.

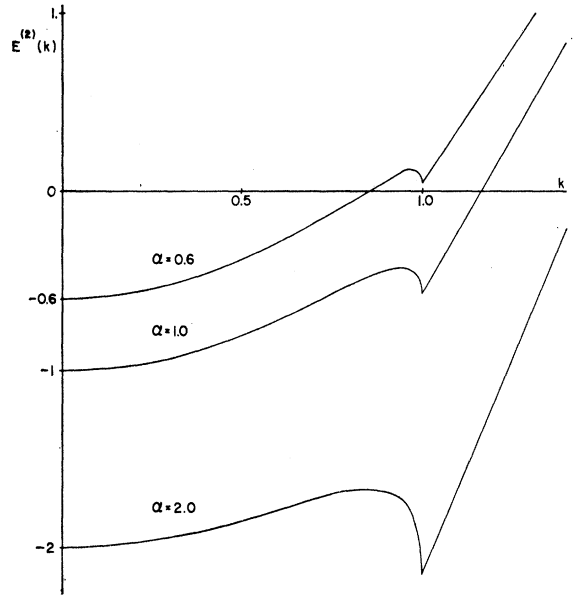

FIG. 1. Polaron energy-momentum plots according to second-order perturbation theory.

Once the problem was formulated in terms of this Hamiltonian, the most natural approach was to treat the interaction as a small perturbation. This constituted a radical departure from earlier work[2] on the problem, which was all in the spirit of what we now call the strong-coupling theory.

The unperturbed energy-momentum relation for an electron is $E^{(0)}(k)=k^2$, and for the first correction to this, second-order perturbation theory gives

$$E^{(2)}(k)=k^2-(\alpha/k)\sin^{-1}k \quad k<1$$
$$=k^2-(\alpha/k)(\pi/2) \quad k>1. \quad (2)$$

This contains the familiar results that

$$E^{(2)}(0)=-\alpha, \quad (3)$$

and

$$m/m^*=(1/1-\alpha/6). \quad (4)$$

In Fig. 1 we plot $E^{(2)}(k)$ for several values of α. Note that $\partial E^{(2)}/\partial k\rightarrow-\infty$ as $k\rightarrow 1$ from below for any value of α, and that for $\alpha\gtrsim 2$ the minimum energy occurs at $k=1$ rather than at $k=0$. It is also clear that the fact that the mass becomes negative at $\alpha=6$ is just an extension of this cusp down to $k=0$. These predictions of perturbation theory are very hard to believe and it is the main purpose of this paper to investigate the cause of these peculiar results, and to indicate what we feel is the correct energy-momentum relation for a polaron.

In Sec. II we will give a qualitative discussion of what the correct energy-momentum relation should be. In Sec. III we will describe a Green's-function theory

[1] H. Fröhlich, H. Pelzer, and S. Zienau, Phil. Mag. 41, 221 (1950).

[2] L. D. Landau, Z. Phys. Sowjetunion 3, 664 (1933). For a current review of the strong-coupling theory, see G. R. Allcock in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963).

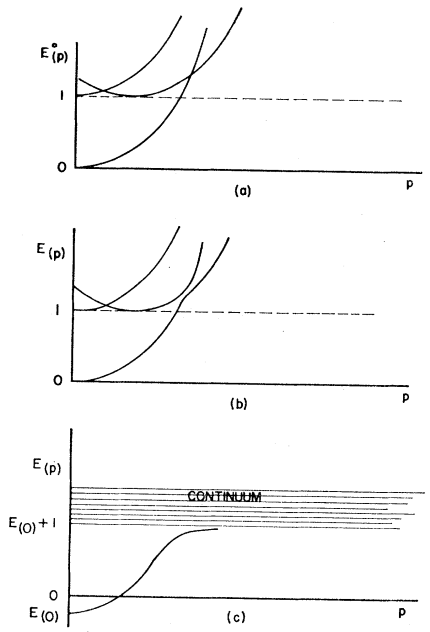

FIG. 2. Polaron energy-momentum plot according to energy-crossing argument.

which has the qualitative features which we believe to be correct.

II. ENERGY CROSSING AND THE TAMM-DANCOFF APPROXIMATION

Schultz has given[3] a simple heuristic argument which indicates the form of $E(k)$. Consider the exact eigenvalues $E^0(k)$ of the noninteracting Hamiltonian [the first two terms in (1)]. Here k is the total wave vector of the eigenstate. Some of the eigenvalues are plotted in Fig. 2(a). Below the line $E^{(0)}(k)=1$ (the phonon energy) there is only one state for each value of k. It is a zero-phonon state. Above $E^{(0)}(k)=1$ there is a quasi-continuum of states (i.e., the states become a continuum in the limit $V\rightarrow\infty$) for each value of k. Only a few of these states are shown in the figure. Suppose we apply a small perturbation which, like the third term in (1), couples only states of the same total momentum. Ordinary perturbation theory applies below the continuum, but in the region above the phonon energy there is degeneracy. A perturbation which couples the two degenerate states shown in 2(a) clearly leads to a splitting similar to that shown in 2(b). Then, if the remaining continuum states are added to the figure, more crossing will result and we expect the final $E(k)$ to have the form shown in 2(c). Note that the continuum now begins at $E=E(0)+1$, since its low-lying states are composed of a polaron plus a free phonon and the free-phonon energy cannot be appreciably affected by the addition of one electron to a macroscopic crystal.

Energy-crossing arguments usually involve only two states, whereas the degeneracy here occurs between the zero-phonon state and a continuum. Therefore, the above argument is perhaps not completely convincing. We can show, however, that the presence of the continuum does not alter the conclusion.

Consider the representation of the Hamiltonian (1) in the unperturbed eigenstates. The submatrix which involves only the zero- and one-phonon states can be diagonalized exactly (we hold the volume finite so that the matrix is discrete). The eigenvalues which lie below 1 are given by

$$E_{\mathrm{TD}}(k)=k^2+(4\pi\alpha/V)\times\textstyle\sum_q 1/q^2(E_{\mathrm{TD}}(k)-1-(\mathbf{k}-\mathbf{q})^2). \quad (5)$$

This is called the Tamm-Dancoff one-quantum cutoff approximation. It was originally applied to the polaron problem by Fröhlich, Pelzer, and Zienau.[1]

In the limit of large volume, (5) reduces to

$$E_{\mathrm{TD}}(k)=k^2-(\alpha/k)\tan^{-1}[k/(1-E_{\mathrm{TD}}(k))^{1/2}];\quad \text{for } E_{\mathrm{TD}}<1 \text{ and } k<k_0, \quad (6)$$

where

$$k_0^2=1+(\pi/2)(\alpha/k_0).$$

Above $E_{\mathrm{TD}}=1$ the exact eigenvalues form a continuum for $V\rightarrow\infty$. The integral which yields (6) does, however, have a principal value in the region $E_{\mathrm{TD}}>1$. The corresponding continuation of $E_{\mathrm{TD}}(k)$ into this region which is

$$E_{\mathrm{TD}}(k)=k^2-(\alpha/k)(\pi/2),$$

and which is shown as a dotted line in Fig. 3, can be thought of as the energy-momentum relation of a quasi-particle with finite lifetime. The solution (6) is an example of a situation in which a degeneracy between one state and a continuum leads to a bend-over in an exact calculation.

Although the Tamm-Dancoff solution is an exact diagonalization of the submatrix, approximating the entire Hamiltonian (1) by this submatrix has serious shortcomings. Therefore, neither the energy crossing

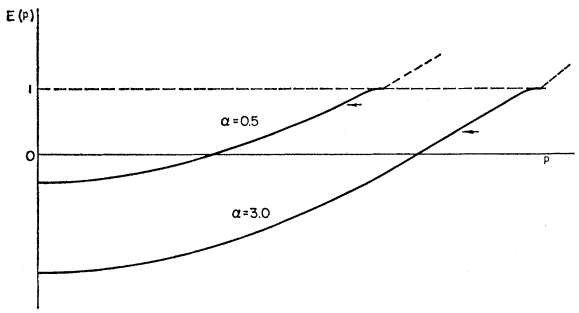

FIG. 3. Polaron energy-momentum plot according to Tamm-Dancoff one-quantum cutoff approximation.

[3] T. D. Schultz, Solid State and Molecular Theory Group, MIT Technical Report No. 9, 1956, (unpublished). Also, G. Whitfield and R. D. Puff, Phys. Letters **10**, 9 (1964).

argument nor the bend-over in (6) have been taken seriously. Two reasons for this are as follows:

(1) The Tamm-Dancoff approximation gives a self-energy which is a higher variational upper bound than the second-order perturbation-theory result, $-\alpha$. Therefore, the approximation has been thought to be a poor one. However, we believe the bend-over to be a reliable feature, because the degenerate states which cause it are treated exactly. The situation here is analogous to that which occurs in the weak binding treatment of band theory, where one considers a free electron perturbed by a periodic potential. Near $k=0$ one uses ordinary perturbation theory, but a degeneracy appears when the wave vector approaches the zone boundary. One must then use degenerate perturbation theory, equivalent to the Tamm-Dancoff approximation, and a bend-over appears which is directly analogous to the one discussed above. The analogy breaks down above the bend-over.

(2) The second difficulty in the Tamm-Dancoff theory is the fact that the bend-over and the beginning of the continuum occur at $E=1$ instead of the anticipated $E=E(0)+1$. The reason for this lies simply in the fact that the Tamm-Dancoff theory allows only one phonon to be present. Hence, a state with one free phonon can contain only a free electron, not a polaron.

In order to see how to correct this defect in the Tamm-Dancoff theory, we first note that Eq. (5) is just the same as second-order perturbation theory with the exception that one of the terms in the energy denominator is the corrected value $E_{\mathrm{TD}}(k)$ instead of k^2. It is then clear that in order to get a theory with singularities at the right places both energies in the denominator must be corrected. Such a theory is developed in the next section.

III. GREEN'S-FUNCTION THEORIES

In this section we will discuss a series of weak-coupling approximations which are arrived at through the technique of thermodynamic Green's functions,[4] and which lead to what we regard to be a reasonable form for the polaron energy-momentum relation.

(a) Definitions

Although everything in this paper is concerned exclusively with one-electron states, we will use the conventional formalism of second quantization in order to discuss the Green's-function approach.

Therefore we rewrite the Hamiltonian (1) treating the electrons in second quantization.

$$H=\sum_k k^2 C_k^\dagger C_k+\sum_q a_q^\dagger a_q + i(4\pi\alpha/V)^{1/2}\sum_q (1/q)(a_{-q}^\dagger - a_q)\rho_{-q}, \quad (1a)$$

where $C_k^\dagger$ creates an electron with wave vector $\mathbf{k}$ and

$$\rho_q \equiv \sum_k C_{k-q}^\dagger C_k.$$

We define the one-particle electron Green's function,

$$G(\mathbf{k},t-t')\equiv -i\langle TC_k(t)C_k^\dagger(t')\rangle; \quad (7)$$

and the phonon Green's function

$$\mathcal{G}(\mathbf{k},t-t')\equiv -i\langle Ta_k(t)a_k^\dagger(t')\rangle. \quad (8)$$

T is the Wick time-ordering operator;

$$\langle A\rangle \equiv (\mathrm{Tr}_{N=0}(e^{-\beta H}A)/\mathrm{Tr}_{N=0}(e^{-\beta H})),$$

and $\mathrm{Tr}_{N=0}$ means the trace over the no-electron states.

For boundary conditions we use the requirements that

$$\mathcal{G}(\mathbf{k},0-t')=\mathcal{G}(\mathbf{k},-i\beta-t') \quad (9)$$

and

$$G(\mathbf{k},t-t')=0 \quad t<t'. \quad (10)$$

Then using the equations of motion we have shown[4] that

$$\mathcal{G}(\mathbf{k},t-t')=\mathcal{G}^0(t-t')=ie^{-i(t-t')}/(e^{-\beta}-1) \quad t>t'$$
$$=-ie^{-i(t-t')}/(e^{\beta}-1) \quad t<t', \quad (11)$$

and that

$$(i(\partial/\partial t)-k^2)G(\mathbf{k},t-t')=\delta(t-t') - i\left(\frac{4\pi\alpha}{V}\right)\sum_q \frac{1}{q^2}\int_{t'}^{t} dt_2[\mathcal{G}^0(t_2-t)+\mathcal{G}^0(t-t_2)] \times\langle TC_{k-q}(t)\rho_q(t_2)C_k^\dagger(t')\rangle. \quad (12)$$

This is the first of an infinite series of equations that relate *electron* Green's functions of different orders, and that involve the phonons only through the known function $\mathcal{G}^0$. In the sense that mixed (electron-phonon) Green's functions have been avoided, we have eliminated the phonons from the problem, and replaced their effect on the electron by a time-dependent potential which can be viewed as describing the electron interacting with itself at previous time. We would like to emphasize that Eq. (12) follows from the Hamiltonian 1(a) without further approximation. This exact elimination of the phonons has been achieved previously in the path-integral formalism.[5]

(b) Tamm-Dancoff

By writing out the equation of motion of the relevant two-electron Green's function,[4] one sees that the lowest order approximation is given by setting

$$\langle TC_{k-q}(t)\rho_q(t_2)C_k^\dagger(t')\rangle \cong -G^0(\mathbf{k}-\mathbf{q},t-t_2)G(\mathbf{k},t_2-t), \quad (13)$$

[4] R. D. Puff and G. D. Whitfield, in *Polarons and Excitons* edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963), p. 171.

[5] R. P. Feynman, Phys. Rev. **97**, 660 (1955).

where

$$G^0(\mathbf{k},t-t')=-ie^{-ik^2(t-t')}, \quad t>t'$$
$$=0 \qquad\qquad t<t' \qquad (14)$$

is the solution to (12) when $\alpha=0$.

Substituting (13) and (14) into (12), Fourier transforming all functions of time, and performing the integral on t_2, we obtain in the $T=0$ limit,

$$G^{-1}(\mathbf{k},\omega)=\omega-k^2-\Sigma_{\mathrm{TD}}(\mathbf{k},\omega). \qquad (15)$$

The Fourier transform of the Green's function is defined by

$$G(\mathbf{k},t-t')=\lim_{\delta\to 0_+}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}G(\mathbf{k},\omega+i\delta)e^{-i\omega(t-t')}.$$

The self-energy $\Sigma(\mathbf{k},\omega)$ is given by

$$\Sigma_{\mathrm{TD}}(k,\omega)=\sum_q (4\pi\alpha/V)(1/q^2)G^0(\mathbf{k}-\mathbf{q},\omega-1). \qquad (16)$$

There is a quasiparticle with energy given by

$$\omega(k)=k^2+\mathrm{Re}\Sigma_{\mathrm{TD}}(k,\omega(k))$$

or

$$\omega(k)=k^2+(4\pi\alpha/V)\mathcal{P}\times\sum_q 1/q^2(\omega(k)-1-(\mathbf{k}-\mathbf{q})^2). \qquad (17)$$

Comparing this with Eq. (5), we see that these are just the solutions to the Tamm-Dancoff one-quantum cutoff. So $\omega(k)=E_{\mathrm{TD}}(k)$.

(c) Hartree-Fock Like Theory

The next reasonable approximation (which in the many-body problem leads to the Hartree-Fock theory) is to assume

$$\langle TC_{k-q}(t)\rho_q(t_2)C_k^{\dagger}(t')\rangle \cong -G(\mathbf{k}-\mathbf{q},t-t_2)G(\mathbf{k},t_2-t'), \qquad (18)$$

which leads to an integro-difference equation[6] for the self-energy,

$$\Sigma_{\mathrm{HF}}(k,\omega)=\sum_q (4\pi\alpha/V)(1/q^2)G(\mathbf{k}-\mathbf{q},\omega-1)$$
$$=(4\pi\alpha/V)\sum_q (1/q^2)\times(\omega-1-(\mathbf{k}-\mathbf{q})^2-\Sigma_{\mathrm{HF}}(\mathbf{k}-\mathbf{q},\omega-1))^{-1}, \qquad (19)$$

and the quasiparticle energy now appears at

$$E_{\mathrm{HF}}(k)=k^2+\mathrm{Re}\Sigma_{\mathrm{HF}}(k,E_{\mathrm{HF}}(k)). \qquad (20)$$

Note that in Eq. (19) the second term in the energy denominator is shifted by the self-energy. This is just the correction that we suggested above would be necessary to make the bend-overs take place at the correct energy. In fact, we can show without solving the integral equation (19), that $\partial E/\partial k\to 0$ as $E\to E(0)+n$ (where $n=1, 2, \cdots$), provided the solution to (19) is reasonably well behaved. To show this we differentiate (20) with respect to k and get

$$\partial E/\partial k=(2k+(\partial\Sigma/\partial k))/(1-(\partial\Sigma/\partial E)).$$

Then, if we assume that for $\omega\approx E(0)$ we can expand $\Sigma(k,\omega)$ in a power series in k [the integrand in (19) is singular near $\omega=E(0)+1$, not $\omega=E(0)$], we see that $\partial\Sigma/\partial E\to\infty$ whenever $\omega\to E(0)+n$ but that $\partial\Sigma/\partial k$ is finite. The assumption that we can expand Σ near $\omega=E(0)$ is *ad hoc*; however, if we cannot make this expansion, we see from Eq. (20) that $E(k)$ would not be quadratic near $k=0$, which would be very unusual.

The integral equation (19) is difficult to solve exactly. In the next section we will find an approximate solution to (19) with the correct qualitative behavior.

(d) Improved Tamm-Dancoff

If on the right of (19) we use the approximation that

$$\Sigma(k,\omega)=V(\omega)+[\gamma(\omega)-1]k^2, \qquad (21)$$

we can then do the integral on q and obtain

$$\Sigma_{\mathrm{ITD}}(k,\omega)=-\frac{\alpha}{k\gamma(\omega-1)}\tan^{-1}\left(\frac{\gamma(\omega-1)k^2}{1-\omega+V(\omega-1)}\right)^{1/2}, \qquad (22)$$

when $1-\omega+V(\omega-1)>0$, and

$$\Sigma_{\mathrm{ITD}}(k,\omega)=-\frac{\alpha}{k\gamma(\omega-1)}\frac{\pi}{2},$$

when $1-\omega+V(\omega-1)<0$.

Expanding both sides of (22) in powers of k and equating the first two coefficients gives $V(\omega)$ and $\gamma(\omega)$ as solutions of the difference equations,

$$V(\omega)=-(\alpha/\gamma^{1/2}(\omega-1)[V(\omega-1)-\omega+1]^{1/2}),$$
$$\gamma(\omega)-1=(\alpha/3)(\gamma^{1/2}(\omega-1)/[V(\omega-1)-\omega+1]^{3/2}). \qquad (23)$$

Equation (23) can be solved numerically with comparative ease. We call Eq. (22) with the solutions of (23) substituted in the right-hand side, the "improved Tamm-Dancoff" (ITD). (Note: It is not just an extension to the two-quantum cutoff.) The quasiparticle energy-momentum relation is then given as the solution of

$$E_{\mathrm{ITD}}(k)=k^2+\mathrm{Re}\Sigma_{\mathrm{ITD}}(k,E_{\mathrm{ITD}}(k)). \qquad (24)$$

One can show directly by differentiating (24) that $\partial E/\partial k\to 0$ as $E\to E(0)+1$. Figure 4 shows plots of $E_{\mathrm{ITD}}(k)$ for several values of the coupling constant. We feel that these constitute a reasonable prediction for the actual energy-momentum relation.

As we have pointed out[4] previously, the "Hartree-Fock-like" theory gives a value of $E(0)$ which is higher than the value given by second-order perturbation theory $(-\alpha)$, which has been shown[7] to be an upper bound to the correct self-energy. The improved Tamm-

[6] This approximation has also been obtained by D. Pines, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963).

[7] T. D. Lee, F. Low, and D. Pines, Phys. Rev. **90**, 297 (1953), and M. Gurari, Phil. Mag. **44**, 329 (1953).

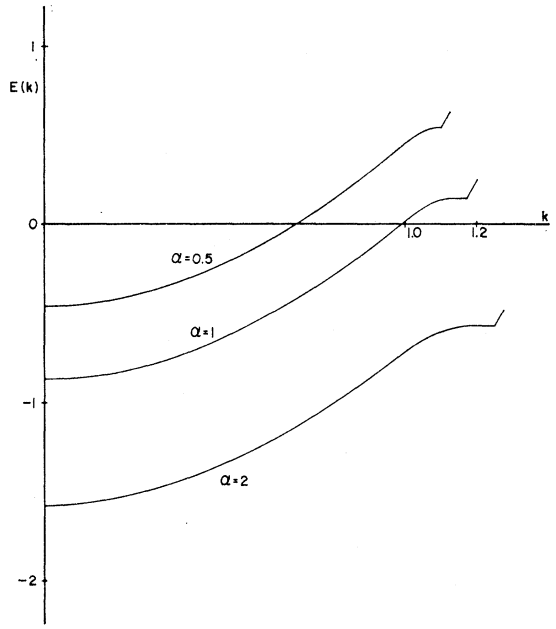

FIG. 4. Polaron energy plots according to the improved Tamm-Dancoff theory.

Dancoff approximation also gives self-energies above $-\alpha$ as is shown in Fig. 4.

If one chooses to use this variational criterion to determine the best theory, one is forced to the conclusion that all the theories we have discussed here are worse than second-order perturbation theory. But for the reasons discussed in part two, we feel that the improved Tamm-Dancoff gives a better theory of the energy-momentum relations. Moreover, in the limit of small coupling constant, all of these theories give the same result, and it is difficult to say at precisely what value of coupling constant these theories break down. For most purposes where the self-energy is not directly used, but where the dynamics of the quasiparticles are of primary interest, the theories described here are probably most appropriate for coupling constants up to 1 or 2.

IV. CONCLUSIONS

The principal conclusion of this paper is that the energy-momentum relation of a polaron has a cusp at $E(k)=E(0)+1$ as shown in Fig. 4. Observing this effect is difficult for several reasons that may not be immediately apparent. One major difficulty with having these bend-overs appear as a qualitative feature in some experiment is the fact that at $E(k)=E(0)+1$ the onset of spontaneous phonon emission occurs and this phenomenon could easily be confused with the fluctuation in the density of states caused by the bend-over.

Other difficulties divide roughly into two groups[8]: those for weak coupling materials like InSb($\alpha \lesssim \frac{1}{10}$), and those for intermediate coupling materials like AgCl and AgBr where $\alpha \approx 2$.

In the weak coupling materials the theory is quite good, and the materials are well understood; however, the bend-overs are very small.

In the intermediate-coupling materials, the bend-overs are quite large but the materials are not nearly as well understood and we are working at the limit of the range of validity of the theory.

The bend-overs take place at the optical-phonon frequency above the ground state. These states are in general occupied at room temperature, since $kT \gtrsim \hbar\omega$. But at these temperatures the states are broadened (according to perturbation theory) by $\Delta E \approx \alpha\hbar\omega\bar{n}$ (where $\bar{n}$ is the average phonon number) and this broadening would in general obscure the bend-over region. At low temperatures the broadening of the quasiparticle energies (due to acoustic-phonon scattering, etc.) would usually be smaller than the bend-over region, but at these temperatures the states of the bend-over region are not normally occupied. (Hot electron experiments have been performed by Masumi[9] on AgCl at 7.6°K, but most of the electrons in these experiments were not hot enough to reach the bend-over region.)

We are now applying the ITD approximation to specific experiments in order to find out where these effects will most easily be observed.

ACKNOWLEDGMENT

The authors would like to thank E-ni Foo for carrying out the numerical solution of the improved Tamm-Dancoff theory.

[8] F. Brown in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963).
[9] T. Masumi, Phys. Rev. **129**, 2564 (1963).