where k is the center-of-mass wave number of the deuteron, s is the spin of the deuteron, i is the spin of the He^3 nucleus, and J is the angular momentum of the compound state. The expression

$$\Gamma_p\Gamma_d/(\Gamma_p+\Gamma_d)^2$$

has the usual meaning and is less than or equal to $\frac{1}{4}$ for all possible choices of Γ_p and Γ_d. In the present case, this reduces to

$$6k^2\sigma/\pi \leqq 2J+1.$$

The measured maximum value of the expression $6k^2\sigma/\pi$ was 2.74 ± 0.49, where the quoted error includes the estimated uncertainties in both energy and cross section. The inequality cannot be satisfied for $J=\frac{1}{2}$ and can be satisfied for $J=\frac{3}{2}$. Thus, it appears that the compound state of Li^5 has total angular momentum $\frac{3}{2}$. Conservation of angular momentum and parity show that this must be a $D_{\frac{3}{2}}$ state. This is in agreement with the assignment of $D_{\frac{3}{2}}$ to the state of He^5 formed in the mirror reaction $H^3(d,n)He^4$.[20]

An analysis of the data at energies above the resonance has not yet been attempted. It may be noted that at the highest energy reached in this experiment, there is no evidence of the double minimum observed in the angular distribution at 10.2 Mev by Allred.[4]

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The Motion of Slow Electrons in a Polar Crystal

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A variational technique is developed to investigate the low-lying energy levels of a conduction electron in a polar crystal. Because of the strong interaction between the electron and the longitudinal optical mode of the lattice vibrations, perturbation-theoretic methods are inapplicable. Our variational technique, which is closely related to the "intermediate coupling" method introduced by Tomonaga, is equivalent to a simple canonical transformation. The use of this transformation enables us to obtain the wave functions and energy levels quite simply. Because the recoil of the electron introduces a correlation between the emission of successive virtual phonons by the electron, our approximation, in which this correlation is neglected, breaks down for very strong electron-phonon coupling. The validity of our approximation is investigated and corrections are found to be small for coupling strengths occurring in typical polar crystals.

I. INTRODUCTION

WHEN an electron in a polar crystal is excited to a low-lying energy level in the conduction band, it interacts strongly with the longitudinal optical mode of the lattice vibrations. More precisely, as the electron moves through the crystal, its Coulomb field displaces the positive and negative ions with respect to one another; the resultant ionic polarization will, in turn, considerably modify the motion of the electron. We may picture the electron as moving through the crystal accompanied by a cloud of phonons (i.e., the associated waves of ionic polarization); the electron plus its associated phonon cloud is known as a polaron.

The theory of the polaron is of more than usual interest because of the mathematical difficulties inherent in any "strong coupling" problem. The dimensionless parameter α, which describes the strength of the electron-phonon coupling, is of the order of magnitude of 3–6 for typical polar crystals. This may be contrasted to the electron-photon coupling constant which is $e^2/\hbar c=1/137$.

The reduction in the electron energy as a consequence of its interaction with the lattice was first computed by Pekar,[1] and by Markham and Seitz,[2] using the adiabatic approximation. Frohlich, Pelzer, and Zienau[3] calculated this energy and the effective mass of the polaron using a one-phonon approximation, which is appropriate provided the electron-lattice coupling is sufficiently weak. However, in most cases of interest, the interaction is so strong that the method of FPZ breaks down; on the other hand, the significant electronic frequencies are comparable to the vibrational frequency of the ionic waves, so that the adiabatic approximation is not applicable.

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[1] S. Pekar, J. Phys. (U.S.S.R.) **10**, 341 (1946).

[2] J. Markham and F. Seitz, Phys. Rev. **74**, 1014 (1948).

[3] Frohlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950), hereinafter referred to as FPZ.

Our approach to this problem is based on a variational technique which does not suffer from either of the above defects.[4] Our essential assumption, following a method first introduced by Tomonaga[5] in treating meson-theoretic problems, is that there is no correlation in the emission of successive virtual phonons by the electron. This assumption appears to have considerable validity for intermediate values of the coupling constant ($\alpha\sim 4$) and for *low-lying* energy states of the system ($P^2/2m\ll\hbar\omega$, where P is the total momentum of the system, m is the mass of the electron, and ω is the frequency of lattice oscillations). However, it seems that our method breaks down in the limit of intermediate momenta ($P^2/2m\sim\hbar\omega$) and very strong coupling. The domain of physical applicability of our method is therefore somewhat restricted.

II. METHOD OF CALCULATION

We adopt the Hamiltonian and notation of Frohlich, Pelzer, and Zienau, in which

$$H=\sum_k \frac{1}{2}\left(M\omega^2 X_k^2+\frac{Y_k^2}{M}\right)$$

$$+\frac{4\pi e}{\sqrt{V}}\sum_k \frac{1}{k}\left(X_k \sin\mathbf{k}\cdot\mathbf{r}+\frac{Y_k}{M}\cos\mathbf{k}\cdot\mathbf{r}\right)+\frac{p^2}{2m}, \quad (1)$$

where ω is the frequency of the longitudinal optical vibrational mode of the lattice oscillation, X_k and Y_k are canonical variables, i.e., $[X_k, Y_{k'}]=\hbar i\delta_{kk'}$, m is the effective mass of the electron (as determined by its interaction with the periodic lattice field), $\mathbf{r}$ and $\mathbf{p}$ are the position and momentum operators of the electron, V is the volume of the crystal, and M is given by

$$M\omega^2=\left[\frac{1}{4\pi}\left(\frac{1}{n^2}-\frac{1}{\epsilon}\right)\right]^{-1}. \quad (2)$$

Here, n and ϵ are the optical index of refraction and the static dielectric constant, respectively. The three terms in this Hamiltonian correspond to the kinetic energy of the electron, the field energy of the phonons, and a term describing the electron-phonon interaction. In using this Hamiltonian we make the following assumptions:

(1) The dielectric may be treated as a continuum. This is a legitimate approximation since the phonons which interact strongly with the electron have a wavelength long compared to the lattice distance, and, as we shall see, the polaron extends over many lattice distances.

(2) The choice of M in Eq. (2) reflects the fact that we consider here only the interaction between the electron and the polarization due to the ionic motion. As pointed out by FPZ, the interaction between the electron and the polarization owing to the bound electrons of the lattice is independent of the electron velocity, and hence would lead only to a constant term in the Hamiltonian, which we may neglect here.

(3) Finally, it is clear that the polarization associated with the acoustic mode of the lattice oscillations, in which neighboring ions vibrate in phase, will be small, so that we need only consider the long wavelength longitudinal optical mode,[6] in which alternate ions vibrate out of phase. The frequency of this mode is essentially independent of wavelength in the range of interest, and is given by $\omega=\omega_t(\epsilon/n^2)^{\frac{1}{2}}$, where ω_t is the experimentally known "reststrahl" frequency for long transverse waves.[7]

We find it convenient to express the Hamiltonian in terms of a new set of variables, a_k and a_k^*, such that

$$a_k=\frac{1}{\sqrt{2}}\left[\left(\frac{M\omega}{\hbar}\right)^{\frac{1}{2}}X_k+i\left(\frac{1}{\hbar M\omega}\right)^{\frac{1}{2}}Y_k\right], \quad (3a)$$

$$a_k^*=\frac{1}{\sqrt{2}}\left[\left(\frac{M\omega}{\hbar}\right)^{\frac{1}{2}}X_k-i\left(\frac{1}{\hbar M\omega}\right)^{\frac{1}{2}}Y_k\right]. \quad (3b)$$

Then

$$H=\sum_k a_k^* a_k\hbar\omega$$

$$+\sum_k\{V_k a_k e^{i\mathbf{k}\cdot\mathbf{r}}+V_k^* a_k^* e^{-i\mathbf{k}\cdot\mathbf{r}}\}+p^2/2m, \quad (4)$$

where we have neglected a zero-point energy $\sum_k \frac{1}{2}\hbar\omega$, and where

$$V_k=-\frac{\hbar\omega i}{k}\left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{4}}\left(\frac{4\pi\alpha}{V}\right)^{\frac{1}{2}}, \quad (5)$$

and

$$\alpha=\frac{e^2}{2\hbar c}\left(\frac{2mc^2}{\hbar\omega}\right)^{\frac{1}{2}}\left(\frac{1}{n^2}-\frac{1}{\epsilon}\right). \quad (6)$$

The dimensionless number α plays the role of a coupling constant for the lattice-electron interaction. a_k and a_k^* may be interpreted as phonon destruction and creation operators, since $[a_k, a_{k'}^*]=\delta_{kk'}$. The wave equation corresponding to (4) is then $H\Phi=E\Phi$.

We shall furthermore find it convenient to take advantage of the fact that the total momentum of our system is a constant of the motion. The total momentum operator is

$$\mathbf{P}_{\text{op}}=\sum_k \hbar\mathbf{k}a_k^* a_k+\mathbf{p},$$

and, of course, commutes with the Hamiltonian, (4). It is, therefore, possible to transform to a representation in which $\mathbf{P}_{\text{op}}$ becomes, a "c" number, and in which the Hamiltonian no longer contains the electron coordinates. The unitary transformation required is $\Phi=S\psi$,

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[4] We have been informed by Professor Frohlich that M. Gurari has developed a method of approach to this problem which is substantially equivalent to ours.

[5] S. Tomonaga, Prog. Theoret. Phys. 2, 6 (1947).

[6] As is well known, any transverse polarization wave has zero divergence and therefore gives rise to no "bound charge."

[7] For the derivation of this relation, see H. Frohlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1949).

where

$$S=\exp[i/h(\mathbf{P}-\textstyle\sum_k a_k{}^*a_k\mathbf{k})\cdot\mathbf{r}]. \tag{7}$$

We find

$$\begin{aligned}\mathbf{P}_{\text{op}}&\rightarrow S^{-1}\mathbf{P}_{\text{op}}S=\mathbf{P}+\mathbf{p},\\ \mathbf{p}&\rightarrow S^{-1}\mathbf{p}S=\mathbf{P}-\textstyle\sum_k \hbar\mathbf{k}a_k{}^*a_k+\mathbf{p},\\ a_k&\rightarrow S^{-1}a_kS=a_ke^{-i\mathbf{k}\cdot\mathbf{r}},\end{aligned} \tag{8}$$

so that

$$\begin{aligned}H\rightarrow\mathcal{H}=S^{-1}HS=\textstyle\sum_k \hbar\omega a_k{}^*a_k+\textstyle\sum_k(V_ka_k+V_k{}^*a_k{}^*)\\ +(\mathbf{P}-\textstyle\sum_k a_k{}^*a_k\mathbf{k}\hbar)^2/2m,\end{aligned} \tag{9}$$

provided we set $\mathbf{p}=0$. The wave equation is now $\mathcal{H}\psi=E\psi$.

Our problem is to calculate for a given momentum P the lowest eigenvalue $E(P)$ of this Hamiltonian. We shall here confine our attention to the low-lying energy levels of the electron, for which $E(P)$ may be well represented by the first two terms of a power series expansion in P^2. Thus $E(P)=E_0+\beta P^2/2+\cdots O(P^4)+\cdots$. The effective mass of the polaron is then β^{-1}.

We use a variational method of calculation, which we will show is equivalent to a simple canonical transformation. We choose for our trial wave function

$$\psi=U\psi_0, \tag{10}$$

where ψ_0 is the eigenstate of the unperturbed Hamiltonian with no phonons present, i.e., the "free" vacuum state. Specifically, ψ_0 is defined by

$$a_k\psi_0=0,\quad(\psi_0,\psi_0)=1, \tag{11a}$$

and

$$U=\exp\{\textstyle\sum_k(a_k{}^*f(\mathbf{k})-a_kf^*(\mathbf{k}))\}, \tag{11b}$$

where $f(\mathbf{k})$ will subsequently be chosen to minimize the energy. It is clear that U is a unitary operator, so that ψ is normalized. Furthermore, viewed as a unitary transformation, U is a displacement operator on a_k and $a_k{}^*$, since

$$U^{-1}a_k{}^*U=a_k{}^*+f^*(\mathbf{k}),\quad U^{-1}a_kU=a_k+f(\mathbf{k}). \tag{12}$$

Our variational calculation, which is based on the use of the state vector ψ [Eq. (10)] is closely related to the approximation introduced by Tomonaga in his treatment of the coupling between mesons and nucleons, which was subsequently named the "intermediate coupling" approximation.

The Tomonaga approximation consists in a variational technique based on the physical assumption that successive virtual phonons (mesons) in the field around the electron (nucleon) are emitted independently, and hence that there is no correlation (i.e., interaction) between different phonons. The mathematical expression of this assumption is that all phonons associated with the ground state of the electron are emitted into the same single phonon state $f(\mathbf{k})$, so that the Fock wave function for that part of the state containing n phonons is a simple product wave function; furthermore, the form of this wave function $f(k)$ is independent of n.

Let us consider a representation in which the Schrödinger function ψ of our system is described by a set of Schrödinger functions corresponding respectively to states of no phonons, one phonon, two phonons, etc. Let $\langle\mathbf{k}_1\mathbf{k}_2\cdots\mathbf{k}_n/\psi\rangle$ be the probability amplitude of finding n phonons of momenta $\mathbf{k}_1$, $\mathbf{k}_2\cdots\mathbf{k}_n$ *respectively* in the phonon field, under the assumption that these phonons are distinguishable.[8] The total probability for finding n phonons in the field around the electron is then given by

$$P(n)=\sum_{k_1}\sum_{k_2}\cdots\sum_{k_n}\langle\mathbf{k}_1\cdots\mathbf{k}_n/\psi\rangle^2. \tag{13}$$

The Tomonaga approximation consists in assuming that $\langle\mathbf{k}_1\cdots\mathbf{k}_n/\psi\rangle$ has the following form:

$$\langle\mathbf{k}_1\cdots\mathbf{k}_n/\psi\rangle=f(\mathbf{k}_1)\cdots f(\mathbf{k}_n)c_n. \tag{14}$$

If the $f(\mathbf{k}_i)$ are normalized, then $P(n)=|c_n|^2$. The form of $f(\mathbf{k})$ and the constants c_n are determined by means of a variational calculation in which the total energy of the system is minimized.

It is easily verified that the use of the state vector (10) is equivalent to setting

$$\begin{aligned}&\langle\mathbf{k}_1\cdots\mathbf{k}_n/\psi\rangle\\ &\qquad=\frac{\exp[-\frac{1}{2}\sum_k|f(k)|^2]}{(n!)^{\frac{1}{2}}}f(\mathbf{k}_1)f(\mathbf{k}_2)\cdots f(\mathbf{k}_n),\end{aligned} \tag{15}$$

whence

$$P(n)=\frac{1}{n!}\exp[-\textstyle\sum_k|f(\mathbf{k})|^2]\{\textstyle\sum_k|f(\mathbf{k})|^2\}^n. \tag{16}$$

Thus we see that our form (15) for $\langle\mathbf{k}_1\cdots\mathbf{k}_n/\psi\rangle$ is not the most general Tomonaga form, since it represents a particular choice of the c_n in Eq. (14). However, it may be shown that up to and including terms of order P^2 in our power series expansion of the energy, no error over and above that of the Tomonaga approximation itself is introduced by our more special assumption, (15). For this reason our calculation of the effective mass of the polaron will be equivalent to that of Lee and Pines who used the Tomonaga approximation.[9]

We seek to minimize the expression for the energy,

$$E=(\psi,H\psi)=(\psi_0,U^{-1}HU\psi_0). \tag{17}$$

In virtue of (12),

$$U^{-1}HU=H_0+H_1, \tag{18}$$

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[8] The correct probability for finding n phonons of momenta k_1, $k_2\cdots k_n$ is $\sum_p\langle k_1\cdots k_n/\psi\rangle^2$ where $\sum_p$ denotes a sum over all permutations of different k's.

[9] T. D. Lee and D. Pines, Phys. Rev. 88, 960 (1952).

with

$$\begin{aligned}H_0=&\frac{(\mathbf{P}-\sum_k a_k^*a_k\mathbf{k}\hbar)^2}{2m}+\sum_k(V_kf(\mathbf{k})+V_k^*f(\mathbf{k}^*))\\&+\frac{\hbar^2}{2m}[\sum_k|f(\mathbf{k})|^2\mathbf{k}]^2\\&+\sum_k|f(\mathbf{k})|^2\left\{\hbar\omega-\frac{\mathbf{k}\cdot\mathbf{P}\hbar}{m}+\frac{k^2}{2m}\hbar^2\right\}\\&+\frac{\hbar^2}{m}\sum_k a_k^*a_k\mathbf{k}\cdot[\sum_{k'}|f(\mathbf{k}')|^2\mathbf{k}']\\&+\sum_k a_k^*\left\{V_k^*+f(\mathbf{k})\left[\hbar\omega-\frac{\hbar\mathbf{k}\cdot\mathbf{P}}{m}+\hbar^2\frac{k^2}{2m}\right.\right.\\&\left.\left.\frac{\hbar^2\mathbf{k}}{m}\cdot(\sum_{k'}|f(\mathbf{k}')|^2\mathbf{k}')\right]\right\}\\&+\sum_k a_k\left\{V_k+f^*(\mathbf{k})\left[\hbar\omega-\hbar\frac{\mathbf{k}\cdot\mathbf{P}}{m}+\hbar^2\frac{k^2}{2m}\right.\right.\\&\left.\left.+\frac{\hbar^2\mathbf{k}}{m}\cdot(\sum_{k'}|f(\mathbf{k}')|^2\mathbf{k}')\right]\right\}+\sum_k a_k^*a_k\hbar\omega,\end{aligned}\tag{19}$$

and

$$\begin{aligned}H_1=&\sum_{kk'}\hbar^2\frac{\mathbf{k}\cdot\mathbf{k}'}{2m}\{a_ka_{k'}f^*(\mathbf{k})f^*(\mathbf{k}')\\&+2a_k^*a_{k'}f(\mathbf{k})f^*(\mathbf{k}')+a_k^*a_{k'}^*f(\mathbf{k})f(\mathbf{k}')\}\\&+\sum_{kk'}\hbar^2\frac{\mathbf{k}\cdot\mathbf{k}'}{m}\{a_k^*a_ka_{k'}f(\mathbf{k}')^*\\&+a_{k'}^*a_k^*a_kf(\mathbf{k}')\}.\end{aligned}\tag{20}$$

Using Eq. (11), we see that

$$\begin{aligned}E=&\frac{P^2}{2m}+\sum_k\{V_kf(\mathbf{k})+V_k^*f^*(\mathbf{k})\}+\frac{\hbar^2}{2m}\{\sum_k|f(\mathbf{k})|^2\mathbf{k}\}^2\\&+\sum_k|f(\mathbf{k})|^2\left\{\hbar\omega-\frac{\mathbf{k}\cdot\mathbf{P}}{m}\hbar+\frac{k^2}{2m}\hbar^2\right\}.\end{aligned}\tag{21}$$

We minimize (21) by setting

$$\delta E/\delta f(\mathbf{k})=\delta E/\delta f^*(\mathbf{k})=0.\tag{22}$$

We find

$$\begin{aligned}V_k+f^*(\mathbf{k})&\left\{\hbar\omega-\frac{\mathbf{k}\cdot\mathbf{P}}{m}\hbar+\frac{k^2}{2m}\hbar^2\right.\\&\left.+\frac{\hbar^2}{m}[\sum_{k'}|f(\mathbf{k}')|^2\mathbf{k}']\cdot\mathbf{k}\right\}=0,\end{aligned}\tag{23}$$

and the appropriate complex conjugate equation for $f(\mathbf{k})$. On comparing (23) and (19) we see that the linear terms (in a_k and a_k^*) of (19) are identically zero provided (23) is satisfied, and hence that H_0 is diagonal in a representation in which $a_k^*a_k$ is diagonal. Thus, our variational calculation is completely equivalent to the use of (19) as our total Hamiltonian, provided $f(k)$ satisfies (23). Since H_0+H_1 differs from H by a unitary transformation, we can obtain an estimate of the accuracy of our variational procedure by a simple perturbation-theoretic estimate of the effect of H_1.

We now seek to evaluate the energy of the lowest state of our system, which is given by Eq. (21), with $f(\mathbf{k})$ satisfying Eq. (23). If we note that the only preferred direction in this problem is that of $\mathbf{P}$, we may conveniently introduce the parameter η defined by

$$\eta\mathbf{P}=\sum_k|f(\mathbf{k})|^2\hbar\mathbf{k}.\tag{24}$$

Equation (23) then becomes

$$f(\mathbf{k})=-V_k^*\bigg/\left[\hbar\omega-\frac{\mathbf{k}\cdot\mathbf{P}}{m}(1-\eta)+\frac{\hbar^2k^2}{2m}\right],\tag{25}$$

and we obtain the following implicit equation for η:

$$\begin{aligned}\eta\mathbf{P}&=\sum_k|f(k)|^2\hbar\mathbf{k}\\&=\sum_k|V_k|^2\hbar\mathbf{k}\bigg/\left[\hbar\omega-\hbar\frac{\mathbf{k}\cdot\mathbf{P}}{m}(1-\eta)+\frac{k^2\hbar^2}{2m}\right]^2.\end{aligned}\tag{26}$$

Using Eq. (5), and transforming the summation in (26) to an integration,[10] we find

$$(\eta-1)^2\eta=\frac{\alpha}{2}\left(\frac{2m\omega\hbar}{P^2}\right)^{\frac{3}{2}}\left\{\sin^{-1}q-\frac{q}{(1-q^2)^{\frac{1}{2}}}\right\},\tag{27}$$

where

$$q=(\eta-1)(P^2/2m\omega\hbar)^{\frac{1}{2}}.\tag{28}$$

We can also obtain the energy in closed form. It turns out to be

$$E=(P^2/2m)(1-\eta^2)-(\alpha\omega\hbar/q)\sin^{-1}q.\tag{29}$$

As long as $P^2/2m$ is sufficiently small so that no spontaneous emission of phonons can occur (roughly $P^2/2m\lesssim\hbar\omega$), Eq. (27) can be solved numerically for a given value of $P^2/2m$, and hence we may obtain $E(P^2)$. As mentioned earlier, we shall here be content to calculate $E(P^2)$ to first order in an expansion in powers of $P^2/2m\hbar\omega$. On doing this, one readily obtains:

$$\eta=\frac{\alpha/6}{1+\alpha/6}+O(P^2/2m\omega\hbar)+\cdots,\tag{30}$$

and

$$\begin{aligned}E=-\alpha\omega\hbar+(P^2/2m)[1/(1+\tfrac{1}{6}\alpha)]&\\+O(P^2/2m\omega\hbar)^2\hbar\omega+\cdots.&\end{aligned}\tag{31}$$

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[10] In carrying out the k integrations we can extend our limits to ±∞, since the contribution to these integrals falls off quite sharply with increasing k.

III. DISCUSSION OF RESULTS

For the slow electrons we have considered, the interaction therefore introduces two effects: (1) All electronic energy levels are reduced by $\alpha\hbar\omega$. (2) The motion of the polaron is that of a free particle with an effective mass $m_{\text{eff}}=m(1+\alpha/6)$. For higher momenta it is clear that the effective mass becomes P-dependent; we have here given only the $P=0$ contribution.

It is of some interest to calculate the mean number of phonons in the cloud around the electron. This is given by

$$N=(\psi, \textstyle\sum_k a_k{}^*a_k\psi)=\sum_k |f(k)|^2, \tag{32}$$

where we have used Eqs. (10)–(12). Hence, by Eq. (25),

$$N=\tfrac{1}{2}\alpha\{(1+[1/(1+\tfrac{1}{6}\alpha)^2]P^2/4m\hbar\omega) \\ +O(P^4/m^2\hbar^2\omega^2). \tag{33}$$

Another physical quantity of interest is the ionic polarization charge density induced by the electron. In order to calculate this, we note that the interaction term in our Hamiltonian [Eq. (1)] is just the potential energy of the electron in the ionic polarization field.[3] The coefficient of $-e$ in this term is therefore the operator which represents the electrostatic potential at a point $\mathbf{r}$. The mean value of this potential when the electron is at some point $\mathbf{r}_e$ is given by

$$\varphi(\mathbf{r}, \mathbf{r}_e)=-(1/e)(\psi_{r_e}, [\textstyle\sum_k V_k a_k e^{i\mathbf{k}\cdot\mathbf{r}} \\ +V_k{}^*a_k{}^*e^{-i\mathbf{k}\cdot\mathbf{r}}]\psi_{r_e}), \tag{34}$$

where

$$\psi_{r_e}=[\exp\{(i/\hbar)\mathbf{r}_e\cdot(\mathbf{P}-\textstyle\sum_k a_k{}^*a_k\hbar\mathbf{k})] \\ \times[\exp\{\textstyle\sum_k a_k{}^*f(\mathbf{k})-a_kf^*(\mathbf{k})\}]\psi_0. \tag{35}$$

[See Eq. (8) and Eq. (10).] The ionic polarization charge density at $\mathbf{r}$ induced by an electron at $\mathbf{r}_e$ is thus

$$\rho(\mathbf{r}, \mathbf{r}_e)=-(1/4\pi)\nabla^2\varphi(\mathbf{r}, \mathbf{r}_e)=-(1/4\pi_e)(\psi_{r_e}, \textstyle\sum_k k^2 \\ \times(V_ka_ke^{i\mathbf{k}\cdot\mathbf{r}}+V_k{}^*a_k{}^*e^{-i\mathbf{k}\cdot\mathbf{r}})\psi_{r_e}). \tag{36}$$

Using (35) we find

$$\begin{aligned}\rho(\mathbf{r}, \mathbf{r}_e)&=-(1/4\pi_e)\textstyle\sum_k k^2\{V_kf(k)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_e)} \\ &\quad+V_k{}^*f^*(k)e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_e)}\} \\ &=-[e\hbar\omega/2V](1/n^2-1/\epsilon) \\ &\quad\times\textstyle\sum_k\{1/[\hbar\omega-\hbar(\mathbf{k}\cdot\mathbf{P}/m)(1-\eta)+(k^2/2m)\hbar^2] \\ &\quad\times\{e^{i\mathbf{k}\cdot\mathbf{r}-\mathbf{r}_e}+e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_e)}\}.\end{aligned} \tag{37}$$

We may immediately calculate the total induced charge,

$$q=\int dr\rho(\mathbf{r}, \mathbf{r}_e)=-e(1/n^2-1/\epsilon), \tag{38}$$

which is the classically expected result for the induced ionic charge on the inner surface of a dielectric medium surrounding a point charge e.

The charge density is, on changing the summation in (37) to an integral,

$$\rho(\mathbf{r}, \mathbf{r}_e)=-e(\hbar\omega/2V)(1/n^2-1/\epsilon)2m/\hbar^2\int dk/(2\pi)^3 \\ \times\left\{\frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_e)}+e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_e)}}{k^2+(2m\omega/\hbar)-2(\mathbf{k}\cdot\mathbf{P}/\hbar)(1-\eta)}\right\}. \tag{39}$$

The integration in (39) is straightforward, and yields

$$\rho(\mathbf{r}, \mathbf{r}_e) \\ =-e\frac{\hbar\omega}{2}\left(\frac{1}{n^2}-\frac{1}{\epsilon}\right)\left(\frac{2m}{\hbar^2}\right)\left\{\left(\frac{1}{2\pi}\right)\cos\left(\frac{(1-\eta)\mathbf{P}\cdot\mathbf{r}-\mathbf{r}_e}{\hbar}\right)\right. \\ \times\frac{\exp[-\{2m\omega/\hbar-(1-\eta)^2P^2/\hbar^2\}^{\frac{1}{2}}|\mathbf{r}-\mathbf{r}_e|]}{|\mathbf{r}-\mathbf{r}_e|}. \tag{40}$$

This induced charge distribution is flattened in the forward and backward directions (with respect to the motion of the polaron). Its mean extension is just $(\hbar/2m\omega)^{\frac{1}{2}}$. This may be considered a good measure of the extension of the polaron. As pointed out by FPZ, since $(\hbar/2m\omega)^{\frac{1}{2}}$ is large with respect to the lattice distance, we are justified in using the continuum approximation in our Hamiltonian.[1]

Comparing our energy, Eq. (31) with that obtained by FPZ, we see that in the limit of weak coupling $\alpha\ll1$, our results reduce to those of FPZ, and that for larger values of α, our result always gives a lower energy. For a typical polar crystal, NaCl, $\alpha=5.2$,[11] $\omega=4.8\times10^{13}$ sec^{-1}, so that we find $E_0=-\alpha\hbar\omega=-0.16$ ev, and $m_{\text{eff}}=1.9m$. In this case FPZ, and also Pekar, obtain $E_0=-0.09$ ev.

Pekar,[12] and Landau and Pekar,[13] using the adiabatic approximation, have found an effective mass for the polaron (in NaCl) of $\sim17m$.[11] However, as might be suspected from Pekar's much higher value of E_0, this high effective mass is due to the lack of applicability of the adiabatic approximation. The condition of validity of the adiabatic approximation is essentially that the frequencies of interest in the problem shall be large compared to the ionic frequency ω. This is, however, not the case for the polarons we have been considering. A convenient measure of the electronic frequencies of interest is provided by the mean kinetic energy of the electron. For $P=0$, one finds

$$\langle T\rangle_{\text{Av}}=\left(\psi, \sum_k\frac{(a_k{}^*a_k\hbar\mathbf{k})^2}{2m}\psi\right)=\sum_k|f(\mathbf{k})|^2\frac{\hbar^2k^2}{2m}=\frac{\alpha\hbar\omega}{2}.$$

Clearly, there is no *external* mechanism, such as exists in a molecule, which can provide the electron with an appreciably higher frequency than ω. The validity of the adiabatic approach is therefore roughly determined

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[11] Here we have taken m to be the mass of a free electron.

[12] S. Pekar, J. Exptl. Theor. Phys. **19**, 796 (1949).

[13] L. Landau and S. Pekar, J. Exptl. Theor. Phys. **18**, 419 (1948).

by $(\alpha/2)^{\frac{1}{2}}$, which is never as large as 2 for polar crystals. Whether the adiabatic approximation applies in principle to the case of extremely large coupling is not clear.

IV. VALIDITY OF OUR METHOD

As is well known, in the limit of infinite electron mass, an exact solution is possible, and follows, in fact, from our canonical transformation. In the case of finite electron mass, the electron's recoil kinetic energy plays an essential role, since it introduces a correlation between the emission of successive virtual phonons. This correlation will tend to limit the validity of our method.

Furthermore, since the Hamiltonian [Eq. (4)] is a function of only four parameters α, P, $\hbar\omega$, and m, of which α is dimensionless, and P^2/m and $\hbar\omega$ are energies, the energy of the system when expanded in powers of P^2 can only be of the form

$$\hbar\omega f_0(\alpha)+P^2/2mf_1(\alpha)+(P^2/2m)^2(1/\hbar\omega)f_2(\alpha)+\cdots.$$

Therefore, in estimating corrections to our results for $f_0(\alpha)$ and $f_1(\alpha)$, we have no dimensional arguments to fall back upon. Our hope is that our variational method has taken into account, to a higher extent than might be obvious, the effect of the correlations introduced by electron recoil, although our wave function is chosen under the assumption of no correlation. This situation is quite analogous to that obtaining in the use of the Hartree-Fock wave functions in the treatment of atomic problems; i.e., although the wave function appears to contain no correlation between different particles (phonons), an "average" effect of the correlation energy is taken into account in the choice of that wave function which minimizes the energy.

The validity of our calculation may best be estimated by calculating the lowest order correction to the energy resulting from that part of the Hamiltonian which we have neglected, *viz.* H_1 [Eq. (20)]. The lowest nonvanishing order in which H_1 affects the energy is the second. The energy shift, which we calculate using conventional perturbation theory, is given by:

$$\Delta E_1=-\sum_n{}'\frac{|(H_1)_{0n}|^2}{E_n-E_0}, \tag{41}$$

where $\sum_n{}'$ is a sum over all the excited states of H_0 to which H_1 has nonvanishing matrix elements. These correspond to two-phonon states. One readily finds:

$$\Delta E_1=-\frac{1}{4m^2}\sum_{k_1k_2}\frac{(\mathbf{k}_1\cdot\mathbf{k}_2)^2|f(\mathbf{k}_1)|^2|f(\mathbf{k}_2)|^2}{\{2\hbar\omega-(\hbar/m)[(\mathbf{k}_1\cdot\mathbf{P})+\hbar(\mathbf{k}_2\cdot\mathbf{P})](1-\eta)+\hbar^2(\mathbf{k}_1+\mathbf{k}_2)^2/2m\}}, \tag{42}$$

with $f(\mathbf{k})$ given by Eq. (23). The indicated summations in (42) have been carried out numerically up to order $P^2/2m\hbar\omega$. The result is:

$$\Delta E_1=-0.007\alpha^2\hbar\omega-0.01\frac{\alpha^2}{(1+\alpha/6)^2}\frac{P^2}{2m}. \tag{43}$$

This is to be compared with our result [Eq. (31)], $E=-\alpha\hbar\omega+(P^2/2m)[1/(1+\frac{1}{6}\alpha)]$. If we set $\alpha=6$, we find a relative correction to the P-independent term of approximately 4 percent; the correction to the $P^2/2m$ term is larger, and is approximately 18 percent. It is perhaps not surprising that the P-dependent correction is larger than the P-independent one, since we might expect that correlation between the emission of successive quanta will play a more important role when a preferred direction exists.

On the whole, therefore, our method provides a reasonable approximation for intermediate values of the coupling constant α, i.e., $\alpha\lesssim 6$. This point of view is confirmed by a detailed one-dimensional calculation of Gross.[14] Gross uses a variational method, with a state vector which may contain zero, one, two, and three phonon parts, to consider the case in which V_k [Eq. (5)] is now independent of k. He finds, for an equivalent coupling constant of 3–4, that the energy of the lowest state, when calculated with a maximum of one, two, and three phonons, respectively, appears to approach a limit which is in substantial agreement with the result we obtain for the same one-dimensional problem using our variational method.

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[14] E. P. Gross, private communication. We are indebted to Dr. Gross for informing us of his results.