[7]W. J. Tomasch, Phys. Rev. 109, 69 (1958).
[8]W. J. Tomasch and J. R. Reitz, Phys. Rev. 111, 757 (1958).
[9]S. Gygax, J. [illegible]. Olsen, and R. J. Kropschot, Phys. Letters 8, 228 (1964).
[10]C. Tyzack and G. Raynor, Trans. Faraday Soc. 50, 675 (1954).
[11]A. Moore, J. Graham, G. K. Williamson, and G. V. Raynor, Acta Met. 3, 579 (1955).
[12]M. F. Merriam, Phys. Rev. Letters 11, 321 (1963); Rev. Mod. Phys. 36, 152 (1964).
[13]E. A. Lynton, B. Serin, and M. Zucker, Phys. Chem. Solids 3, 165 (1957).
[14]J. E. Gueths, C. A. Reynolds, and M. A. Mitchell, Phys. Rev. 150, 346 (1966).
[15]F. V. Burckbuchler, D. Markowitz, and C. A. Reynolds, Phys. Rev. 175, 543 (1968).
[16]G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. 114, 719 (1959).
[17]D. P. Seraphim, C. Chiou, and D. J. Quinn, Acta Met. 9, 861 (1961).
[18]Y. Ohtsuka, Y. Shibuya, and T. Fukuroi, Sci. Res. Inst. Tohoku Univ. Ser. A (Japan) 15, 67 (1963).
[19]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[20]Here "linear effects" is used in the MK context. Clem actually uses the older terminology "valence effects," which we shall avoid as being misleading.
[21]Supplied by United Mineral and Chemical Corp., New York, N. Y.
[22]Precision bore Pyrex capillary with a specified i.d. of 2.000 ± 0.005 mm, supplied by the Wilmad Glass Co., Buena, N. J.
[23]C. A. Reynolds, B. Serin, and L. Nesbitt, Phys. Rev. 84, 691 (1951).
[24]The pressure over the helium bath was measured using a Texas Instruments Model 141 servo-driven fused-quartz precision pressure gauge, and a bath height correction was made to determine the pressure at the sample position.
[25]1958 He^4 scale of temperatures.
[26]T. P. Sheahen, Phys. Rev. 149, 368 (1966).
[27]D. K. Finnemore and D. E. Mapother, Phys. Rev. 140, A507 (1965).
[28]D. Markowitz, Ph.D. thesis, University of Illinois, 1963 (unpublished).
[29]P. N. Dheer, Proc. Roy. Soc. (London) A260, 333 (1961).
[30]K. R. Lyall and J. F. Cochran, Phys. Rev. 159, 517 (1967).
[31]K. Fossheim and J. R. Leibowitz, Phys. Letters 22, 140 (1966).
[32]A. C. E. Sinclair, Proc. Phys. Soc. (London) 92, 962 (1967).
[33]V. D. Fil', O. A. Shevchenko, and P. A. Bezugly, Zh. Eksperim. i Teor. Fiz. 52, 891 (1967) [Soviet Phys. JETP 25, 587 (1967)].
[34]R. W. Morse, T. Olsen, and J. D. Gavenda, Phys. Rev. Letters 3, 15 (1959).
[35]It should be noted that the ac field method used in this investigation was not applicable to the detection of normal ⟷ super transitions for temperatures more than 80 m°K below T_c in the pure samples, since eddy currents set up by the changing flux change and caused the transition to be poorly defined.

PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Polaron Mass. I. The Free Polaron

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An approximate calculation is made of the polaron effective mass as defined by Fröhlich. The approach taken is a variational one based on an extended version of Höhler's ansatz in which the trial state function employed is an exact eigenfunction of the total wave vector of the polaron. The effective mass obtained simulates the Feynman-Schultz results while the corresponding polaron self-energy is fairly accurate but inferior to the result of Feynman and Schultz.

I. DEFINITION OF PROBLEM

In a description of the motion of a single conduction electron in an ionic semiconductive crystal, Fröhlich[1] develops a Hamiltonian for a system consisting of the electron interacting with the polarization field resulting from the long-wavelength longitudinal optical modes of the crystal. The Hamiltonian is given by

$$H(\alpha) = -\frac{\partial^2}{\partial \vec{r}^2} + \sum_{\vec{v}} b_{\vec{v}}^{\dagger} b_{\vec{v}} + i\,(4\pi\alpha/S)^{1/2} \times \sum_{\vec{v}} [(1/v)\,(b_{\vec{v}}^{\dagger} e^{-i\vec{v}\cdot\vec{r}} - b_{\vec{v}} e^{+i\vec{v}\cdot\vec{r}})], \quad (1)$$

where $\vec{r}$ is the coordinate of the electron, $b_{\vec{v}}^{\dagger}$ and $b_{\vec{v}}$ are bosonic creation and destruction operators of a polarization field quantum of wave vector $\vec{v}$, α is a dimensionless coupling constant characteristic of the crystal, and S is the normalization volume. The limit $S \to \infty$ is to be taken with

$$\lim_{S\to\infty} \sum_{\vec{v}} = \frac{S}{8\pi^3} \int d^3v \,. \quad (2)$$

In the derivation of Eq. (1), the crystal is treated as a continuous medium and it is assumed that, in the absence of the polarization field, the conduction electron moves as a free particle with a Bloch mass m. It is also assumed that the long-wavelength longitudinal optical modes, which interact significantly with the electron, all have a common angular frequency ω. A natural unit system is employed in which $\hbar = \omega = 2m = 1$.

The name "polaron" has been given to the entity consisting of the Bloch conduction electron together with its accompanying nonradiative polarization field. Accordingly, Fröhlich defines the polaron self-energy $E_0(\alpha)$, and the polaron effective mass $\mu(\alpha)$:

$$E_0(\alpha, \vec{k}) = E_0(\alpha) + [1/\mu(\alpha)]k^2 + O(k^4), \tag{3}$$

where $E_0(\alpha, \vec{k})$ is the least eigenvalue of $H(\alpha)$ whose corresponding eigenfunction is simultaneously an eigenfunction of the conserved total wave vector

$$\vec{K} = \frac{1}{i}\frac{\partial}{\partial \vec{r}} + \sum_{\vec{v}} \vec{v} b_{\vec{v}}^{\dagger} b_{\vec{v}}, \tag{4}$$

with corresponding eigenvalue $\vec{k}$. In ordinary units the self-energy is $E_0(\alpha)\hbar\omega$ and the effective mass is $\mu(\alpha)m$.

Fröhlich's definition of the polaron effective mass is of special interest because it is based upon the rigorously valid law of conservation of total wave vector, and as such is properly defined apart from any method of approximation. Moreover, it is shown in the sequel to this paper that Fröhlich's polaron effective mass is what is measured in a cyclotron resonance experiment at low magnetic fields.

The problem of determining the self-energy and effective mass of the polaron as functions of the polaron coupling constant α is of long-standing interest because it serves as an ideal testing ground for some types of field-theoretical methods of approximation. The Lee-Low-Pines[2] variational calculation yields

$$E_0(\alpha) = -\alpha \tag{5}$$

and

$$\mu(\alpha) = 1 + \tfrac{1}{6}\alpha. \tag{6}$$

These results (also obtainable by perturbation theory) are exactly correct to first order in α in the limit of weak coupling. The strong-coupling variational calculations of Landau[3] and Pekar[4] yield

$$E_0(\alpha) = -a\alpha^2 \tag{7}$$

and

$$\mu'(\alpha) = b\alpha^4 + 1, \tag{8}$$

with

$$a \approx 0.10 \quad \text{and} \quad b \approx 0.02. \tag{9}$$

The analytic form of Eq. (7) is asymptotically correct.[5] The effective mass μ' given by Eq. (8) is based on a generalized definition of effective mass, which is equivalent to Fröhlich's definition only if the wave function employed is an eigenfunction of the total wave vector. The Landau-Pekar trial wave function represents the electron as bound to a fictitious trapping point. Such a wave function is not an eigenfunction of the total wave vector. The Feynman-Schultz[6,7] results for the self-energy and their effective mass agree both with the Lee-Low-Pines results for weak coupling and with the Landau-Pekar results for strong coupling and possess smooth transitional behavior for intermediate coupling. Their effective mass, however, is based upon still another definition which is convenient within the path-integral formulation which they employ.

The question arises as to whether Fröhlich's effective mass is approximated by the results obtained on the basis of these alternative definitions. It is the purpose of this paper to provide some insight into the answer to this question by displaying a trial polaron ground-state function which is an exact eigenfunction of the total wave vector, which yields results for Fröhlich's effective mass which are similar to the Feynman-Schultz effective mass, and which at the same time yields reasonable results for the polaron self-energy.

II. SOLUTION

In order to evaluate Fröhlich's polaron effective mass for strong coupling, Höhler[8] employs a trial state function given by

$$\Psi_H = S^{-1/2} \int d^3y\, e^{i\vec{k}\cdot\vec{y}} \Psi_0(\vec{r}-\vec{y}, \vec{y}), \tag{10}$$

where $\Psi_0(\vec{r}-\vec{y}, \vec{y})$ has the form of a Landau-Pekar trial state function in which $\vec{y}$ is the point to which the electron is bound in the Landau-Pekar description. Such a state function is given by

$$\Psi_0(\vec{r}-\vec{y}, \vec{y}) = \Omega(\vec{r}-\vec{y})\,\Phi(\vec{y}), \tag{11}$$

where

$$\Omega(\vec{r}-\vec{y}) = e^{-(\vec{r}-\vec{y})^2/\beta^2} \tag{12}$$

is a ground-state bound-electron wave function in which β is a variational parameter and where $\Phi(\vec{y})$ is a polarization field state function (independent of the electron coordinate $\vec{r}$) chosen to minimize the expectation value of H with respect to $\Psi_0(\vec{r}-\vec{y}, \vec{y})$. The resulting choice is

$$\Phi(\vec{y}) = e^{-i\sum_{\vec{v}} f_{\vec{v}}(\vec{y}) b_{\vec{v}}^{\dagger}}\, \Phi_0, \tag{13}$$

where

$$f_{\vec{v}}(\vec{y}) = (4\pi\alpha/S)^{1/2} v^{-1} e^{(-1/8)v^2\beta^2 - i\vec{v}\cdot\vec{y}}, \tag{14}$$

and where Φ_0 is the polarization-field vacuum state.

Höhler's trial state function Ψ_H is such a linear combination of Landau-Pekar state functions that the result is an exact eigenfunction of the total wave vector with corresponding eigenvalue equal to $\vec{k}$. For asymptotically strong coupling, Höhler's results, based on Ψ_H, agree with the Landau-Pekar self-energy, but yield just one-half of the Landau-Pekar effective-mass value.

Of greater generality than Ψ_H, however, any state function of the form

$$\Psi = \int d^3y\, \Psi_{\vec{k}}(\vec{r},\vec{y})\,\Phi(\vec{y}), \tag{15}$$

where

$$\Psi_{\vec{k}}(\vec{r},\vec{y}) = S^{-1/2}\exp\{i\vec{k}\cdot[t\vec{y}+(1-t)\vec{r}\,]\}\cdot\Omega(\vec{r}-\vec{y}) \tag{16}$$

is also an exact eigenfunction of the total wave-vector operator with corresponding eigenvalue equal to $\vec{k}$, regardless of the value of the variational parameter t so introduced.[9] Expression (16) has the form of the ground-state wave function for a two-particle system consisting of the electron with coordinate $\vec{r}$ and a fictitious particle with coordinate $\vec{y}$ bound together by a simple harmonic attraction. The variational parameter t represents the ratio of mass of the fictitious particle to the total mass of the two-particle system. Höhler's state function Ψ_H represents the special case of Ψ for which the mass of the fictitious particle is infinite and thus $t=1$. For $\vec{k}=0$, Ψ and Ψ_H are equivalent. As a result, the polaron self-energy based on Ψ must reproduce Höhler's polaron self-energy. On the other hand, the effective mass based on Ψ differs from Höhler's result.

To obtain the self-energy $E_0(\alpha)$ and Frölich's effective mass $\mu(\alpha)$ corresponding to the trial state function Ψ, one must first calculate the expectation value $E_0(\alpha,\vec{k})$ of H as given by Eq. (1) with respect to Ψ as given by Eqs. (15), (16), and (12)–(14). Next, $E_0(\alpha,\vec{k})$ must be expanded in a power series about $\vec{k}=0$ through second order to obtain $E_0(\alpha)$ and $1/\mu(\alpha)$ as the leading coefficients, in accordance with Eq. (3). The result for $E_0(\alpha)$ depends upon β, but not upon t, and $1/\mu(\alpha)$ depends upon both β and t. One may then determine the optimum values of β and t by minimizing $E_0(\alpha)$ with respect to β and by minimizing $1/\mu(\alpha)$ with respect to t. Such a method is justified, since for arbitrary values of $\vec{k}$, $E_0(\alpha,\vec{k})$ must be greater than the exact least eigenvalue of the operator H restricted to operation in the eigenspace of the total wave-vector operator with corresponding eigenvalue equal to $\vec{k}$.

III. RESULTS

The preceding procedure ultimately leads to the following results for approximating the polaron self-energy $E_0(\alpha)$ and Fröhlich's polaron effective mass $\mu(\alpha)$, wherein it remains to minimize the self-energy with respect to the variational parameter $C\equiv 2/\beta$:

$$E_0(\alpha) = I_1/I_0 \tag{17}$$

and

$$\mu(\alpha) = [1-\tfrac{2}{3}I_4^2/(I_1I_2-I_0I_3)]^{-1}, \tag{18}$$

where

$$\begin{aligned} I_0 &= \int_0^\infty R(x)\,dx, \quad I_1 = \int_0^\infty Q(x)R(x)\,dx, \\ I_2 &= \int_0^\infty x^2R(x)\,dx, \quad I_3 = \int_0^\infty x^2Q(x)R(x)\,dx, \\ I_4 &= \int_0^\infty xV(x)R(x)\,dx, \end{aligned} \tag{19}$$

with

$$\begin{aligned} R(x) &= x^2\exp[-\tfrac{1}{2}x^2+\tfrac{1}{2}\alpha Cx^{-1}\phi(x)-\alpha C/\sqrt{\pi}], \\ Q(x) &= -2\alpha Cx^{-1}\phi(\tfrac{1}{2}x) \\ &\quad +\tfrac{1}{4}\alpha Cx^{-1}[2\phi(x)+C^2x\phi'(x)]-V^2(x), \\ V(x) &= \tfrac{1}{4}\alpha C^2x^{-2}[x\phi'(x)-\phi(x)], \end{aligned} \tag{20}$$

wherein

$$\begin{aligned} \phi(x) &= \int_0^x \phi'(y)\,dy, \\ \phi'(x) &= (2/\sqrt{\pi})\,e^{-x^2}. \end{aligned} \tag{21}$$

Numerical minimization of $E_0(\alpha)$ with respect to C yields the results given in Table I. Figures 1 and 2 show graphically the results for the self-energy and effective mass. For comparison, in the same figures are shown the corresponding results of Lee, Low, and Pines, of Landau and Pekar, and of Feynman and Schultz.

In the limit of strong coupling, both the self-energy and the effective mass agree with the Landau-Pekar results. In the limit of weak coupling,

$$E_0(\alpha) = -0.778\alpha + O(\alpha^2) \tag{22}$$

TABLE I. Self-energy and effective mass of the polaron as functions of the polaron coupling constant.

Coupling constant α	Variational parameter $C(\pm 1\%)$	Self-energy $E_0(\pm 1\%)$	Effective mass $\mu(\pm 2\%)$
1	1.96	− 0.776	1.21
2	2.02	− 1.59	1.53
4	2.22	− 3.40	2.89
6	2.59	− 5.59	8.05
7	2.87	− 6.92	16.2
8	3.18	− 8.46	33.9
9	3.54	−10.2	67.4
10	3.90	−12.2	121
11	4.26	−14.4	198
13	4.99	−19.5	440
15	5.73	−25.4	840
20	7.49	−44.0	2900

and

$$\mu(\alpha) = 1 + 0.179\alpha + O(\alpha^2), \tag{23}$$

which may be compared with the exact weak-coupling expansions

$$E_0(\alpha) = -\alpha + O(\alpha^2) \tag{24}$$

and

$$\mu(\alpha) = 1 + (\tfrac{1}{6} \approx 0.167)\alpha + O(\alpha^2). \tag{25}$$

IV. REFINEMENT

The preceding presentation is a simplification of a more refined treatment based on a trial polaron state function obtained by replacing Eq. (14) by the more general form

$$f_{\vec{v}}(\vec{y}) = p^2(4\pi\alpha/S)^{1/2}[v(1+2\xi\vec{k}\cdot\vec{v}+\eta^2 v^2)]^{-1}$$

$$\times \exp[-\tfrac{1}{8}(1-\zeta)^2\beta^2 v^2 - i(1-\zeta)\vec{v}\cdot\vec{y}], \tag{26}$$

where p, ξ, η, and ζ are additional variational parameters. By setting $p = 1$ and $\eta = \xi = \zeta = 0$ in Eq. (26), one recovers Eq. (14). Although the total number of variational parameters of this refined model is six, all but two of them may be eliminated analytically. A study[10] of this refined treatment reveals that for all values of α less than a critical value of about 7, the variationally optimum value of ζ and η is exactly unity, in which case the results degenerate to the Lee-Low-Pines results which are correct to first order in α for weak coupling. However, if the variational parameters are constrained according to the equation

$$(1-\zeta)/(\eta\beta) = (4/3\sqrt{\pi})[\alpha + 2(e^{-\alpha/2} - 1)], \tag{27}$$

it is found that the resulting self-energy and effective mass go smoothly from weak-coupling values which are correct to first order in α, to strong-coupling values which agree with the Landau-Pekar results. The self-energy obtained with this constraint is superior to the result given in Table I but inferior to Feynman's for all values of α and the effective mass is slightly less than Feynman's. Since the effective-mass result prior to refinement is slightly greater than Feynman's result, it is therefore apparent that the variational parameters of the refined model could be constrained in such a way to reproduce the Feynman-Schultz effective mass and simultaneously give a self-energy which is slightly superior to the result given in Table I.

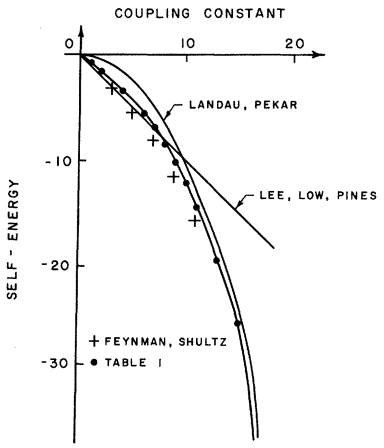

FIG. 1. Self-energy of the polaron as a function of the polaron coupling constant.

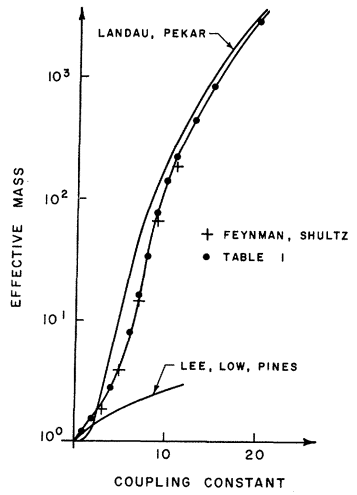

FIG. 2. Effective mass of the polaron as a function of the polaron coupling constant.

V. CONCLUSION

The polaron effective mass is defined by Fröhlich on the basis of the exact law of conservation of the polaron total wave vector. It is known that for weak coupling, the Fröhlich effective mass is given by $\mu = 1 + \frac{1}{6}\alpha$ correctly to first order in the polaron coupling constant α. The calculations of the effective mass by Landau and Pekar for strong coupling and by Feynman and Schultz for all coupling strengths are both based on alternative definitions which are convenient to their methods of approximation. The Feynman-Schultz effective-mass results agrees to first order in α with the correct result for weak coupling, agrees with the Landau-Pekar result for strong coupling, and provides a smooth transitional behavior for intermediate coupling. The contention that the effective-mass calculations based on these alternative definitions do approximate the Fröhlich effective mass is supported here by the display of a polaron state function which is an exact eigenfunction of the polaron total wave vector, which yields

fairly accurate polaron self-energies, and which yields a Fröhlich effective mass, closely simulating the Feynman-Schultz effective-mass approximation.

An alternative approach to obtaining the polaron effective mass is provided by a study of the cyclotron motion of a polaron which is discussed in the sequel to this paper.

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[1]H. Fröhlich, Advan. Phys. 3, 325 (1954).
[2]T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. 90, 297 (1953).
[3]L. Landau, Phys. Z. Sowjetunion 3, 664 (1933).
[4]S. I. Pekar, J. Phys. USSR 10, 341 (1946).
[5]E. H. Lieb and K. Yamazaki, Phys. Rev. 111, 728 (1958).
[6]R. P. Feynman, Phys. Rev. 97, 660 (1955).
[7]T. D. Schultz, Phys. Rev. 116, 526 (1959).
[8]G. Höhler, Z. Naturforsch. 9A, 801 (1954).
[9]G. R. Allcock, Advan. Phys. 5, 413 (1956).
[10]B. U. Stewart, Ph. D. thesis, Louisiana State University, 1971 (unpublished).

PHYSICAL REVIEW B VOLUME 2, NUMBER 10 15 NOVEMBER 1970

Spin Exchange in Excitons, the Quasicubic Model and Deformation Potentials in II-VI Compounds

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The effect of the spin-exchange interaction between electron and hole is investigated for the case of excitons originating from one of the p-like valence bands and an s-like conduction band, as is the case for IIb-VIb compounds. A general exciton matrix is constructed, starting from the work of Pikus. It includes spin-orbit, crystal-field, spin-exchange, and deformation-potential interactions. Use of this matrix then allows a theoretical fit to our experimental data which describes the shift of exciton levels under uniaxial pressure in ZnO, CdS, and CdSe. This fit results in the determination of six deformation potentials, two spin-orbit parameters, the crystal-field parameter, and the exchange parameter. The general theory, when adapted to the zinc-blende structure, allows us to fit our data on cubic ZnS and ZnSe, resulting in a determination of two deformation potentials and the spin-exchange parameter for each compound.

I. INTRODUCTION

The phenomenon of free excitons in semiconducting crystals has been a subject of considerable interest for many years and has been summarized in general by Knox,[1] and in particular with respect to group II-VI compounds by Reynolds *et al.*[2] It has always been clear that the exciton properties are closely related to the fundamental properties of the materials in which they were observed. For the interpretation of these exciton spectra, one usually considers that an exciton is composed of two particles: an electron in a conduction band and a hole in a valence band which are bound together by the Coulombic interaction. It is customarily assumed further that the j-j coupling scheme holds for these exciton states in the framework of the one-electron energy-band model. Thus, multiple structures in the exciton spectra are attributed to the excitonic transitions arising from the split-off valence bands. One usually equates the energy difference between two excitons in a cubic material such as zinc-blende ZnS with the spin-orbit splitting of its valence band. In wurtzite CdS, Hopfield related the observed energy differences of the three free excitons observed near the fundamental gap to the spin-orbit and crystal-field parameters of the CdS valence band on the basis of the quasicubic model.[3] This procedure has been generally followed in the in-