

masses were determined from the average separations in $1/H$ of the derivative maxima. For the bisectrix axis the cyclotron effective masses were determined from the position of the combined Landau-spin flip transitions in conjunction with spin resonance transition. This procedure has the obvious advantage of being less sensitive to the effect of a finite relaxation time and the additional effects that the presence of other carriers can have on the position of the inflection point. The A-K behavior with the field normal to the surface and circular polarization does not permit a discrimination between holes and electrons. For this one still has to rely on the location of an inflection point for the two senses of polarization.

The origin of the unexplained structure associated with the binary and bisectrix axes is not understood. Aubrey⁸ has seen, in addition to the holes observed by Brandt¹⁵ and Galt *et al.*,² peaks which he attributes to

a very light hole band. An examination of our data for the presence of these light holes is inconclusive. They do not correspond to our unexplained structure. We have inspected the binary axis data for possible subharmonics of the heavier mass electron. Such peaks, which would be related to the departure of the conduction from parabolicity, have not been found.

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Many-Particle Theory of Impurity States in Polar Crystals

STEPHEN J. NETTEL

Research Laboratory, International Business Machines Corporation, Rüschlikon-Zurich, Switzerland

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An attempt is made to generalize to polar semiconductors, Kohn's many-particle approach to the theory of shallow impurity states in nonpolar crystals. Nuclear coordinates are included as dynamic variables. The impurity state is described as a linear combination of exact many-particle eigenfunctions that correspond to the motion of a polaron through the impurity-free crystal. The resulting effective dielectric constant is likewise identified as the usual static constant, by considering the interaction between an electron bound by an infinitesimal impurity charge and a small classical charge fixed at a large displacement from the impurity. Corrections to the resulting hydrogenic equation arise from the need to include real phonon states. These corrections are estimated for substances with weak electron-lattice coupling only. The corrections are found small for most III-V semiconductors. They are rather more serious for substances such as CdAs₂ and CdS, that have somewhat stronger coupling, suggesting a limitation to the applicability of the theory. In an Appendix an interpretation of the new formal contribution to the effective dielectric constant is given in terms of the motion of the ion cores.

1. INTRODUCTION

IN a well-known paper Kohn has given a many-particle theory of impurity states in nonpolar crystals, which gives a rigorous basis to the customary effective-mass treatment of the problem.¹ Recently, impurity states in polar crystals have become of wide experimental interest.²⁻⁴ The theoretical analysis of the polar problem has likewise already received attention.^{5,6} The present paper attempts to show that

a generalization of Kohn's theory to polar crystals is possible, at any rate for crystals in which the coupling between conduction electrons and phonons is weak.

A number of measurements have been made via electrical properties of the impurity activation energy in substances with relatively weak electron phonon coupling: in indium-doped cadmium sulphide (CdS), for example, by Piper and Halsted,² and in CdAs₂ by Fischler and Koenig.³ In both materials investigators have found rough agreement with the hydrogenic ionization energies providing that the static rather than the high-frequency dielectric constant was used.⁷ The

¹ W. Kohn, Phys. Rev. **105**, 509 (1957).

² W. W. Piper and R. E. Halstead, *Proceedings of the International Conference on Semiconductors, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961).

³ Quoted by: W. J. Turner, A. S. Fischler, and W. E. Reese, Suppl. J. Appl. Phys. **32**, 2241 (1961).

⁴ H. P. R. Frederikse, Suppl. J. Appl. Phys. **32**, 2211 (1961).

⁵ R. Kubo, J. Phys. Soc. Japan **3**, 254 (1948).

⁶ P. M. Platzman, Phys. Rev. **125**, 1961 (1962).

⁷ In CdS one finds agreement to within 15% with the hydrogenic formula (reference 2). In CdAs₂ agreement to within 5% has recently been found by a direct measurement of the static dielectric constant. R. D. Brown and S. H. Koenig, Phys. Letters **2**, 309 (1962).

activation energy of GaAs is likewise becoming known⁸; this substance is currently undergoing intensive study in a number of laboratories.

An early analysis of impurity states in polar crystals was made by Kubo,⁵ who employed a description of the system with no correlation between the instantaneous position of the "extra" electron and the lattice polarization. In a recent paper Platzmann has treated the problem on the basis of an effective-mass model, with the Fröhlich interaction between electron and lattice.⁶ Energies are obtained variationally using the Feynman path integral technique. A treatment considering the (transformed) electron lattice interaction as a perturbation is also carried out.

Kohn's many-particle approach reconciles the use of an independent particle model on the one hand, and a dielectric constant on the other.¹ His calculation can be viewed as consisting of two parts. In the first, the wave function of the system is expanded in terms of the exact many-particle eigenfunctions $\Psi_{n\mathbf{K}}$ of the crystal with an extra electron but without the extra impurity charge. The expansion is inserted into the Schrödinger equation for the system, which includes interactions between the impurity charge (taken as infinitesimally small) and the charges of the crystal. There, then, emerges quite naturally a hydrogenic wave equation, which has its Coulomb potential reduced in the ratio of an effective dielectric constant, κ^* , that has a formal definition in terms of the many-particle functions, $\Psi_{n\mathbf{K}}$. In the second calculation a strongly plausible definition of the true dielectric constant κ is given in terms of the interaction between an electron trapped by the infinitesimal impurity charge and a distant classical point charge, negative and small. κ^* and κ are then shown to be identical. There is a second paper by Kohn,⁹ with which no contact will be made here, where the identity of κ^* , defined as in the first paper, and κ , now defined in terms of the interaction of two distant point charges, is established using Brueckner-Goldstone linked-cluster theory.

It is helpful to consider the problem, an impurity fixed in its polar crystal interacting with a moving carrier, from a classical physics point of view. First, one notes that since the impurity charge, $-qe$ (q will always be positive and e , in general, the electronic charge), is stationary, it is shielded by the full static polarization. This is not generally true of the moving carrier, charge e , as its motion may be too rapid for the ionic polarization to follow. However, some reflection shows that, regardless of the extent to which the moving charge is shielded, the interaction between the charges will be $-qe^2/(\kappa R)$, where κ is the static dielectric constant, and R the separation of the charges. One forms the picture of a polaron with its characteristic mass and self-energy interacting via the static dielectric

constant with the fixed impurity. This suggests that it may be possible to follow Kohn's analysis for nonpolar crystals, and to describe the impurity state as a combination of a relatively small number of exact eigenfunctions of the impurity-free crystal (polaron states). At zero temperature these eigenfunctions would cover a range of propagation vectors, but would contain no real phonons. Evidently, describing the "extra electron" by a wave packet may bring about some changes in the phonon dressing associated with the component eigenfunctions. These changes may be expected to yield corrections to a hydrogenic equation to an extent difficult to predict in advance.

In the next section the two calculations of Kohn's paper¹ modified to allow for the motion of the ions are repeated. Coordinates of motion for the nuclei are introduced into the Hamiltonian and into the generalized wave functions. The results are similar to Kohn's with several interesting new features. A hydrogenic equation, however, with the expected corrections is obtained; the dielectric constant which appears is the static one in accordance with experimental indications, the effective mass is the corrected polaron mass. These results are rather in agreement with Platzman's perturbation calculation.⁶ The corrections to the hydrogenic equation are taken up in Sec. 3. They are shown to be small when the coupling between the electron and the lattice is sufficiently weak. The formal definition of the static dielectric constant in terms of the many-particle functions contains a new term, as it turns out, the direct contribution of the ionic polarization. This term is discussed in the Appendix.

2. IMPURITY STATE AND DIELECTRIC CONSTANT

Let there be N valence electrons in the regular insulating crystal, and let \mathbf{r}_i , $i=1, 2, \dots, N+1$, be the position vectors of the $(N+1)$ loosely bound electrons taken to be in the crystal. Let \mathbf{R}_{ls} be the equilibrium position of an ion of type s in the unit cell l of the crystal, \mathbf{u}_{ls} the displacement of the ion from \mathbf{R}_{ls} , and \mathbf{X}_{ls} its total displacement ($\mathbf{R}_{ls} + \mathbf{u}_{ls}$). Let $H(\mathbf{r}_i, \mathbf{u}_{ls})$ be the complete Hamiltonian of the impurity-free crystal. That is, H contains the kinetic energies of both the normal crystal ion cores and of the $(N+1)$ electrons, and the mutual Coulomb interactions between all these charges. $\Psi_{n\mathbf{K}}(\mathbf{r}_1 \cdots \mathbf{r}_{N+1}, \cdots \mathbf{u}_{ls} \cdots)$ are the eigenfunctions of H . Like H they contain ion-core coordinates \mathbf{u} in addition to electronic coordinates as dynamic variables.

$$H\Psi_{n\mathbf{K}} = E_{n\mathbf{K}}\Psi_{n\mathbf{K}}. \quad (1)$$

Here $E_{n\mathbf{K}}$ are the eigenvalues; the subscripts n, \mathbf{K} will be defined shortly. The $\Psi_{n\mathbf{K}}$ will be taken as orthonormal when the integration extends over electronic and nuclear variables.

The functions $\Psi_{n\mathbf{K}}$ have the following generalized symmetry:

⁸ D. J. Oliver, Phys. Rev. **127**, 1045 (1962).

⁹ W. Kohn, Phys. Rev. **110**, 857 (1958).

$$\Psi_{n\mathbf{K}}(\mathbf{r}_1+\mathbf{T}, \dots \mathbf{r}_{N+1}+\mathbf{T}, \dots \mathbf{u}_{(ls-\mathbf{T})} \dots) \\ = \exp(i\mathbf{K} \cdot \mathbf{T}) \Psi_{n\mathbf{K}}(\mathbf{r}_1, \dots \mathbf{r}_{N+1}, \dots \mathbf{u}_{ls} \dots), \quad (2)$$

where \mathbf{T} is one of the fundamental translational vectors of the lattice, $\mathbf{u}_{(ls-\mathbf{T})}$ is the displacement from equilibrium of the ion at $(\mathbf{R}_{ls}-\mathbf{T})$, and \mathbf{K} is in virtue of (2) the propagation vector of $\Psi_{n\mathbf{K}}$. Equation (2) is a consequence of the fact that if all the electrons are advanced by \mathbf{T} , and the ion-core configuration as defined by the \mathbf{u} 's is likewise advanced by \mathbf{T} ,

$$(\mathbf{r}_i \rightarrow \mathbf{r}_i + \mathbf{T}, \mathbf{u}_{ls} \rightarrow \mathbf{u}_{(ls-\mathbf{T})}),$$

the Coulomb interactions in H and, hence, H itself remains invariant.

Following Kohn one writes

$$\Psi_{n\mathbf{K}} = e^{i\mathbf{K} \cdot \mathbf{r}_1} \Phi_{n\mathbf{K}}, \quad (3)$$

where $\Phi_{n\mathbf{K}}$ is to remain invariant under the total translation \mathbf{T} . \mathbf{K} is to be restricted to the first Brillouin zone. The remaining specification of the state is contained in n . From the shallow impurity problem in nonpolar crystals¹⁰ one can presume that the inclusion of conduction bands higher than the first introduces but small corrections, which will not be considered here. Accordingly, the index n will be used to indicate, roughly speaking, the phonon content of the eigenstates $\Psi_{n\mathbf{K}}$, all of which will be taken to lie in the same "electronic band."

Again following Kohn, the set of lowest states, $n=0$, will in the vicinity of the energy minimum be taken to have a quasi-continuous energy spectrum of the form (cubic symmetry assumed),

$$E_{0\mathbf{K}} = E_{00} + \hbar^2 K^2 / (2m^*). \quad (4)$$

One likes to think that cyclotron resonance truly yields m^* as defined in (4). In an independent-particle model m^* would correspond to the polaron effective mass, i.e., it would include the effect of the phonon "dressing" of the electron.

The impurity atom, assumed to be fixed at the origin and to carry a positive excess charge $(-qe)$, will give rise to a perturbation U ($U = U_1 + U_2$):

$$U_1 = -qe^2 \sum_{i=1}^{N+1} r_i^{-1}, \quad (5a)$$

$$U_2 = qe^2 \sum_{l,s} Z_s |X_{ls}|^{-1}, \quad (5b)$$

where $-eZ_s$ is the charge carried by an ion-core of type s .

The eigenfunctions Ψ of the crystal with the impurity are expanded thus:

$$\Psi = \sum_{n,\mathbf{K}} A_{n\mathbf{K}} \Psi_{n\mathbf{K}}. \quad (6)$$

Substitution into the Schrödinger equation,

$$(H+U)\Psi = E\Psi, \quad (7)$$

gives a set of equations having exactly the same form as those given by Kohn.¹¹ One now makes the rather crucial assumption, treated in Sec. 3, that the coefficients $A_{n\mathbf{K}}$, when $n \neq 0$, associated with states having one or more real phonons, are relatively small compared with the ground-state coefficients, $A_{0\mathbf{K}}$. Solution by iteration then yields

$$(E_{0\mathbf{K}} - E)A_{0\mathbf{K}} + \sum_{\mathbf{K}'} \left[(0\mathbf{K}|U|0\mathbf{K}') \right. \\ \left. + \sum_{\mathbf{K}''} \sum_{n \neq 0} \frac{(0\mathbf{K}|U|n\mathbf{K}'')(n\mathbf{K}''|U|0\mathbf{K}')}{E - E_{n\mathbf{K}''} - (n\mathbf{K}''|U|n\mathbf{K}'')} \right] A_{0\mathbf{K}'} = 0. \quad (8)$$

The round brackets in (8) indicate integration over nuclear as well as over electronic coordinates.

Since in the state $\Psi_{0\mathbf{K}}$ the extra electron is distributed uniformly throughout the crystal, the expectation value $(0\mathbf{K}|U|0\mathbf{K})$ will differ by a negligible amount from the interaction of the impurity charge with the perfect N -electron insulator. In the same way the second-order term

$$\sum_{\mathbf{K}''} \sum_{n \neq 0} \frac{(0\mathbf{K}|U|n\mathbf{K}'')(n\mathbf{K}''|U|0\mathbf{K})}{E - E_{n\mathbf{K}''}}$$

is, essentially, the self-energy of the impurity charge, i.e., its interaction with its own polarization.¹² These terms will appear as additive constants to the various energy eigenvalues.

To calculate $(0\mathbf{K}|U|0\mathbf{K}')$ ($\mathbf{K} \neq \mathbf{K}'$), one Fourier analyzes Eqs. (5), and draws on Eq. (3) to get

$$(0\mathbf{K}|U|0\mathbf{K}') = \frac{4\pi qe^2}{V} \\ \times \sum_{\mathbf{p} \neq 0} \frac{1}{p^2} \left[-(N+1)(\Phi_{0\mathbf{K}}^* \Phi_{0\mathbf{K}'} e^{i(\mathbf{p}+\mathbf{K}'-\mathbf{K}) \cdot \mathbf{r}_1}) \right. \\ \left. + \sum_{l,s} Z_s (\Phi_{0\mathbf{K}}^* \Phi_{0\mathbf{K}'} \exp[i\mathbf{p} \cdot (\mathbf{X}_{ls} - \mathbf{r}_1)] \right. \\ \left. \times \exp[i(\mathbf{p}+\mathbf{K}'-\mathbf{K}) \cdot \mathbf{r}_1] \right]. \quad (9)$$

Here V is the volume of the crystal, and the \mathbf{p} are all nonvanishing vectors compatible with periodic boundary conditions for U . The factor $(N+1)$ originates from the equivalence of all crystal electrons.

Now, in view of Eq. (2),

$$\Phi_{0\mathbf{K}}^* \Phi_{0\mathbf{K}'} \exp[i\mathbf{p} \cdot (\mathbf{X}_{ls} - \mathbf{r}_1)]|_{\mathbf{r}_1 \dots \mathbf{r}_{N+1}, \dots \mathbf{u}_{ls} \dots} \\ = \Phi_{0\mathbf{K}}^* \Phi_{0\mathbf{K}'} \exp\{i\mathbf{p} \cdot [\mathbf{X}_{(ls+\mathbf{T})} \\ - (\mathbf{r}_1 + \mathbf{T})]\}|_{\mathbf{r}_1+\mathbf{T}, \dots \mathbf{r}_{N+1}+\mathbf{T}, \dots \mathbf{u}_{(ls-\mathbf{T})} \dots} \quad (10)$$

¹¹ A more complete discussion of many points raised in the present section will be found in reference 1.

¹⁰ J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955); or see W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 5, p. 257.

¹² Since it is E rather than $E_{0\mathbf{K}}$ that appears in the denominator, this term could, conceivably, cause a shift in the operative mass m^* .

That is, the right term in (10) is to be evaluated for a configuration shifted by \mathbf{T} relative to that for the left term. This allows one to make the following expansion in reciprocal lattice vectors \mathbf{K}_ν indicating lattice periodicity in \mathbf{r}_1 :

$$\sum_{l,s} Z_s (\Phi_{0\mathbf{K}}^* \Phi_{0\mathbf{K}'} \exp[i\mathbf{p} \cdot (\mathbf{X}_{ls} - \mathbf{r}_1)])' = V^{-1} \sum_{\nu} \rho_{i\nu}(\mathbf{K}, \mathbf{K}', \mathbf{p}) e^{i\mathbf{K}_\nu \cdot \mathbf{r}_1}. \quad (11)$$

The primed parentheses on the left indicate integration over all dynamic variables except \mathbf{r}_1 . Evidently, one can also make the expansion

$$(\Phi_{0\mathbf{K}}^* \Phi_{0\mathbf{K}})' = V^{-1} \sum_{\nu} \rho_{e\nu}(\mathbf{K}, \mathbf{K}') e^{i\mathbf{K}_\nu \cdot \mathbf{r}_1}. \quad (12)$$

Equations (11) and (12) are substituted into (9), and on integrating over \mathbf{r}_1 , one finds that

$$(0\mathbf{K} | U | 0\mathbf{K}') = -4\pi q e^2 V^{-1} \sum_{\nu} |\mathbf{K} - \mathbf{K}' - \mathbf{K}_\nu|^{-2} \times [(N+1)\rho_{e\nu}(\mathbf{K}, \mathbf{K}') - \rho_{i\nu}(\mathbf{K}, \mathbf{K}', \mathbf{K} - \mathbf{K}' - \mathbf{K}_\nu)]. \quad (13)$$

It will turn out that as for the nonpolar case the significant matrix elements are those with K and K' small compared to K_ν . Accordingly, only the terms $\nu=0$ in (15) will be retained. Furthermore, $\rho_{e\nu}$ and $\rho_{i\nu}$ will be replaced by their limiting values as \mathbf{K}' and \mathbf{K} approach zero, but remain distinct, a point taken up in the Appendix. An effective dielectric constant, κ^* , is now defined by

$$\lim_{\mathbf{K}, \mathbf{K}' \rightarrow 0; \mathbf{K} \neq \mathbf{K}'} [(N+1)\rho_{e0}(\mathbf{K}, \mathbf{K}') - \rho_{i0}(\mathbf{K}, \mathbf{K}', \mathbf{K} - \mathbf{K}')] = 1/\kappa^*, \quad (14)$$

where ρ_{e0} and ρ_{i0} can be obtained by inverting Eqs. (11) and (12). Equation (14) will be seen as a generalization of Kohn's original definition.¹ Thus, finally one has

$$(0\mathbf{K} | U | 0\mathbf{K}') = -4\pi q e^2 (V\kappa^*)^{-1} |\mathbf{K} - \mathbf{K}'|^{-2}. \quad (15)$$

If for the moment one drops the terms of second order in U in Eq. (8), and sets

$$E - (0\mathbf{K} | U | 0\mathbf{K}) - E_{00} = E', \quad (16)$$

then, with the help of (4) and (15), one finds

$$\left(\frac{\hbar^2 K^2}{2m^*} - E' \right) A_{0\mathbf{K}} - \frac{4\pi q e^2}{V\kappa^*} \sum_{\mathbf{K}' \neq \mathbf{K}} \frac{A_{0\mathbf{K}'}}{|\mathbf{K} - \mathbf{K}'|^2} = 0. \quad (17)$$

This will be recognized as a hydrogenic Schrödinger equation in K space, with parameters m^* for the electron mass, and κ^* for the dielectric constant. Also to be remembered is the restriction on K to lie in the first Brillouin zone. (See reference 1 for transformation to real space.)

The argument that is used in the nonpolar problem can be adapted to make the identity of κ^* , as defined in (14), and κ , the true static dielectric constant, extremely plausible. If the impurity charge qe is allowed to become vanishingly small (so that the

relevant region in K space describing the orbit tends to zero), then, as in the nonpolar problem, Eq. (17) becomes, indeed, exact. The accompanying solution of (17), Ψ_0 ,

$$\Psi_0 = \sum_{\mathbf{K}} A_{0\mathbf{K}} \Psi_{0\mathbf{K}}, \quad (18)$$

becomes the exact solution of the impurity problem.

The interaction between the impurity charge $-qe$ and its trapped electron on the one hand, and a small negative point charge Qe displaced by R from the impurity on the other, where R is large relative to the dimensions of the impurity state, will be

$$Qe^2/(\kappa R), \quad (19)$$

since q is assumed infinitesimal, (19) is to be taken as the definition of κ .

The charge Qe introduces the perturbation

$$H' = Qe^2 \sum_{i=1}^{N+1} |\mathbf{r}_i - \mathbf{R}|^{-1} - Qe^2 \sum_{ls} Z_s |\mathbf{X}_{ls} - \mathbf{R}|^{-1}. \quad (20)$$

The procedure now is to calculate the first-order shift in energy ($\Psi_0, H' \Psi_0$). The calculation proceeds by essentially the same steps as those given in Kohn's work. Equation (20) is Fourier analyzed, substitution is made from both Eqs. (11) and (12), and the integral over \mathbf{r}_1 is taken. If one omits the term, $\sum_{\mathbf{K}} |A_{0\mathbf{K}}|^2 \times (0\mathbf{K} | H' | 0\mathbf{K})$, the self-energy of the charge Qe , one finds, as R gets very large and q very small, the result:

$$(\Psi_0, H' \Psi_0) = Qe^2/(\kappa^* R), \quad (21)$$

where κ^* is exactly as defined in Eq. (14). Comparison with Eq. (19) establishes the identity of κ and κ^* .

3. CORRECTIONS TO HYDROGENIC EQUATION

In the introduction, considerations were outlined which suggested that the terms of second order in U in Eq. (8) are small compared to the first-order terms. Indeed, if this is not the case then the perturbation scheme that has been applied to solve the exact equations for the $A_{n\mathbf{K}}$'s will not give convergent results. On the other hand, if the second-order terms are small, then reliable results can be obtained even if the terms are not known very precisely, since they are corrections to first-order terms which are well known. In this section the second-order terms will be estimated for substances that have relatively weak electron-lattice coupling (coupling constant $\alpha < 1$). It will turn out that these terms are, indeed, small providing that the coupling is particularly weak, as in the III-V semiconductors. The estimates are possible because wave functions are readily available. It is thought that the second-order terms will remain small even as the coupling strength is increased somewhat, providing that orbital radii of the impurity states remain large compared to characteristic polaron radii. For one thing it is energetically unfavorable to build by polarization a potential well about a large crystal volume. In addi-

tion, the relatively large orbital radius is equivalent to a slow orbital angular velocity relative to the circular frequency of the optical lattice modes.

It is thought that the second-order terms can be estimated sufficiently reliably in terms of a one-electron model. To make the model consistent with the many electron formalism one must imagine one-electron crystal functions, say $e^{i\mathbf{K}\cdot\mathbf{r}}\chi_0$, where \mathbf{r} are the electron's coordinates and χ_0 is a nuclear function, as being multiplied by a function $\phi_r(r_2, r_3, \dots, r_{N+1}, u)$, which has the effect of surrounding the electron by a proper electronic polarization. That is, within an r independent constant,

$$\int \phi_r^2(-qe^2) \sum_{i=2}^{N+1} (1/r_i) d\tau_2 \dots \tau_{N+1} = -\frac{qe^2}{\tau} (\kappa_\infty^{-1} - 1), \quad (22)$$

where κ_∞ is the optical dielectric constant.

In this spirit the Hamiltonian for the impurity-free crystal assumes the well-known form¹³:

$$H = -[\hbar^2/(2m)]\nabla^2 + \hbar\omega \sum_{\mathbf{w}} b_{\mathbf{w}}^* b_{\mathbf{w}} + igV^{-1/2} \sum_{\mathbf{w}} w^{-1} [b_{\mathbf{w}}^* \exp(-i\mathbf{w}\cdot\mathbf{r}) - b_{\mathbf{w}} \exp(i\mathbf{w}\cdot\mathbf{r})], \quad (23a)$$

$$g = (4\pi\alpha)^{1/2} [\hbar^5\omega^3/(2m)]^{1/4}. \quad (23b)$$

The first term is the kinetic energy of the electron in the periodic potential of the crystal, the second the energy of the optical longitudinal vibrations of the lattice, ω being roughly the common frequency for these modes. $b_{\mathbf{w}}^*$ and $b_{\mathbf{w}}$ are the creation and annihilation operators for phonons of wave number \mathbf{w} . The last term is the electron-lattice interaction, which is proportional to the square root of the usual coupling constant α .¹³

Formally, the second-order corrections also include excitations of acoustic phonons. It might be emphasized that the energy denominators appearing explicitly in the corrections associated with these excitations do not contain any poles, since in E is included its decrease by the first-order (hydrogenic) binding energy. Nevertheless, a detailed treatment of this question would be rather tricky.¹⁴ For the present one assumes that the effects of the acoustic excitations are small as compared to the more appreciable polar effects being sought. This can, perhaps, be inferred from the experimental results in silicon and germanium, where phonon excitations do not appear to show up.

For every substance there is a characteristic momentum vector K_p , $\hbar^2 K_p^2/(2m) = \hbar\omega$. It turns out that that for the substances of special interest here the

¹³ G. R. Allcock, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 412.

¹⁴ In a subsequent paper we hope to investigate in some detail the ground-state polaron functions for weak coupling with propagation vectors K , $\hbar^2 K^2/(2m) > \hbar\omega$. This will allow one to subtract out explicitly the contribution of the unexcited states $|0K''\rangle$ from the sum $\sum_{\mathbf{K}'', n} (0K|U|n\mathbf{K}'')(n\mathbf{K}''|U|0K')$. (One may think of this sum as being also roughly representation independent with regards only to states $|n\mathbf{K}''\rangle$ at about the same energy.)

TABLE I. Experimental and calculated characteristics for representative polar crystals.

	GaAs ^{a,b}	CdAs ^{c,d}	CdS ^e
$A(K_p)/A(0)$	0.03	0.12	0.08
α	0.06	~ 0.7	~ 0.5
κ_∞	13.5	10	5.2
κ	11.6	18.5	9.2
E _q . (30)	0.10 α	0.3 α	0.4 α

^a See reference 8.

^b H. Ehrenreich, Phys. Rev. **120**, 1951 (1960). In attempting to obtain agreement of the ionization energy with experiment the (yet unknown) temperature dependence of the dielectric constant may be important.

^c See reference 3.

^d See reference 7.

^e See reference 2.

"polaron radius,"¹⁵ $1/K_p$, is smallish compared to the corresponding orbital radius, so that the ratio $A(K_p)/A(0)$ of Fourier components characterizing hydrogen like $1s$ orbitals is relatively small. Using experimental values for the effective masses and static dielectric constants one finds the ratios listed in the second line of Table I. The next three lines of the table give some relevant experimental information.

Only second-order terms with $K, K' < K_p$ will be calculated.¹⁴ In view of the listed ratios, $A(K_p)/A(0)$, it is these which are of principal interest. For $K < K_p$, and $\alpha < 1$, one may write for an eigenfunction $\Psi_{0\mathbf{K}}$ of the Hamiltonian given in (23) the first-order perturbation expression:

$$\Psi_{0\mathbf{K}} = \frac{e^{i\mathbf{K}\cdot\mathbf{r}}}{V^{1/2}} \chi_0 - \frac{ig}{V} \sum_{\mathbf{w}} \frac{\exp[i(\mathbf{K}-\mathbf{w})\cdot\mathbf{r}] b_{\mathbf{w}}^* \chi_0}{w \{ \hbar\omega + \hbar^2/(2m) [(\mathbf{K}-\mathbf{w})^2 - K^2] \}}, \quad (24)$$

where χ_0 is again the ground state of the lattice oscillators. To estimate the second-order terms, the excited polaron functions $\Psi_{n\mathbf{K}''}$ are simply replaced by unperturbed states, $\exp[i(\mathbf{K}''-\mathbf{w})\cdot\mathbf{r}] b_{\mathbf{w}}^* \chi_0$. Excited states in the unperturbed representation having more than one phonon will give no contribution to the second-order terms, providing that the interaction of the impurity with the ion cores is linearized. One now draws on Eqs. (5a), (8), (16), and (22). Making some obvious approximations in integrating over angles, and substituting first-order (hydrogenic) ionization energies for E' , one finds:

$$\begin{aligned} \sum_{\mathbf{K}''} \sum_{n \neq 0} \frac{(0\mathbf{K}|U|n\mathbf{K}'')(n\mathbf{K}''|U|0\mathbf{K}')}{E - E_{n\mathbf{K}''} - (n\mathbf{K}''|U|n\mathbf{K}')} &\sim - \sum_{\mathbf{K}''} \\ &\times \sum_{\mathbf{w}} \frac{(0\mathbf{K}| - qe^2/(\kappa_\infty r) | \mathbf{w}\mathbf{K}'') (\mathbf{w}\mathbf{K}'' | - qe^2/(\kappa_\infty r) | 0\mathbf{K}')}{-E' + \hbar\omega + \hbar^2/(2m) (\mathbf{K}'' - \mathbf{w})^2} \\ &= 0.2\alpha \frac{qe^2}{r_0 \kappa_\infty \hbar\omega} \left(\frac{-4\pi qe^2}{V \kappa_\infty |\mathbf{K} - \mathbf{K}'| K_0} \right). \quad (25) \end{aligned}$$

¹⁵ H. Fröhlich, H. Pelzer, and S. Zienau, Phil. Mag. **41**, 221 (1950).

Here r_0 is meant to be the Bohr radius of the impurity orbital, and K_0 the reciprocal of r_0 , ($K_0 r_0 = 1$).

The term in brackets in (25) can be taken as roughly the equivalent of the first-order term $(\mathbf{K}|U|\mathbf{K}')$, see Eq. (15). The last line in Table I lists the numerical value of the factor to the left of the bracketed term. It is interesting to note that this factor contains essentially the ratio of impurity binding to optical phonon energy.

The result (25) is evidently not quite right for a number of reasons. The true excited polaron states $\Psi_{n\mathbf{K}'}$ contain with $[\exp i(\mathbf{K}'' - \mathbf{w}) \cdot \mathbf{r}] b_w^* \chi_0$ admixtures of other states of the same momentum, in particular of $(\exp i\mathbf{K}'' \cdot \mathbf{r}) \chi_0$.¹⁴ In addition, U_2 , the interaction of the impurity with the ion cores, has not been included in calculating the matrix elements. However, owing to the partial shielding of the extra electron by the ions, one might expect the latter interaction to numerically reduce the final result of a more complete evaluation. Nevertheless, it is believed that (25) is of the correct order of magnitude, and that it allows one to draw conclusions as follows.

For a range of III-V semiconductors, typified by GaAs, that have coupling constants $\alpha < 0.1$ the perturbation scheme suggested here converges rapidly. The second-order terms are small compared to first-order ones, being corrections of one or several percent. Accordingly, the impurity orbitals and the associated eigenvalues can be found with good reliability. In a calculation of the ionization energy in, say, GaAs (0.009 eV) the switch from κ_∞ to κ will have an appreciable effect of about 35%, whereas the second-order terms may be expected to lead to a correction that is hardly significant. (The change in a calculated effective mass arising from the phonon dressing of the electron, $\alpha m/6$, would also be unimportant here.)

In substances such as CdAs₂ or CdS where $\alpha \sim 0.5$ the situation is less satisfactory. From the present estimates one cannot conclude with certainty that the perturbation scheme converges. Nevertheless, leaning on experimental information already mentioned one can, perhaps, expect that there will be a slow convergence, and that the present theory will give an accounting here as well.

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APPENDIX

The Static Dielectric Constant

The term ρ_{i0} defined in (11) and appearing in the definition (14) of κ^* can be understood in terms of crystal functions having a generalized tight-binding form (the functions appearing in "small polaron" theories¹⁶). From (3) and (11), and remembering that $X_{ls} = R_{ls} + u_{ls}$, one has

$$\rho_{i0}(\mathbf{K}, \mathbf{K}', \mathbf{K} - \mathbf{K}') = \sum_{l,s} Z_s e^{i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{R}_{ls}} (\Psi_{0\mathbf{K}}^* \Psi_{0\mathbf{K}'} e^{i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{u}_{ls}}). \quad (\text{A1})$$

The tight-binding functions, $\Psi_{0\mathbf{K}}$, describing a polar insulator with an extra electron have the general form:

$$\Psi_{0\mathbf{K}} = L^{-1/2} \sum_{l,s} e^{i\mathbf{K} \cdot \mathbf{R}_{ls}} W_{ls}(\mathbf{r}_1 \cdots \mathbf{r}_{N+1}, \mathbf{u}) \chi_0(\mathbf{u})_{ls}. \quad (\text{A2})$$

Here W_{ls} is a suitable $(N+1)$ electron function, which concentrates the extra electron in the vicinity of the crystal ion at R_{ls} . χ_0 describes the ground-state oscillations of the ion cores, the \mathbf{u} indicates the dependence of both W and χ_0 on all nuclear coordinates, and L is the number of ions in the crystal. The subscripts ls attached to χ_0 indicate the dependence, to become clearer shortly, of χ_0 on the location of the extra electron. Since W_{ls} is assumed to diminish rapidly when the "extra" electron leaves the vicinity of R_{ls} the function (A2) possesses a proper correlation between the extra electron and the ionic configuration. Furthermore, if under the total translation \mathbf{T} , W_{ls} goes into $W_{ls-\mathbf{T}}$, $\Psi_{0\mathbf{K}}$ will satisfy the symmetry requirement of Eq. (2).¹⁷

If now (A2) is substituted into (A1), cross terms are neglected, and the integration over all electronic coordinates is carried out, one obtains

$$\rho_{i0}(\mathbf{K}, \mathbf{K}') = L^{-1} \sum_{l,s,l',s'} Z_s e^{i(\mathbf{K} - \mathbf{K}') \cdot (\mathbf{R}_{ls} - \mathbf{R}_{l's'})} \times \int \chi_0^2(\mathbf{u})_{l's'} e^{i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{u}_{ls}} d\mathbf{u}, \quad (\text{A3})$$

where the integral is over all nuclear coordinate space.

$\chi_0(\mathbf{u})_{l's'}$ is most naturally chosen as the usual ground-state oscillator function, the oscillations, however, being about displaced equilibrium positions, there being a separate equilibrium configuration, $l's'$, for each location $\mathbf{R}_{l's'}$ of the extra charge concentration.¹⁶ Thus, if $\mathbf{x}_{ls}(l's')$ is the equilibrium displacement of the ion ls appropriate for the configuration $l's'$, it will be assumed that for sufficiently large R ($\mathbf{R} = \mathbf{R}_{ls} - \mathbf{R}_{l's'}$), \mathbf{x}_{ls} satisfies the inverse square law:

$$\mathbf{x}_{ls}(l's') = \mathbf{x}(\mathbf{R}) = f_s \mathbf{R} R^{-3}, \quad (\text{A4})$$

¹⁶ See, for instance, S. J. Nettel, Phys. Rev. **121**, 425 (1961).

¹⁷ For example, for a one-electron function one could choose $W_{ls} = w(\mathbf{r} - \mathbf{X}_{ls})$, where $w(r)$ is a bound atomic orbital.

where f_s is a proportionality constant, which depends (also in sign), on s , the type of ion being displaced. \mathbf{R} runs over all regular interionic displacements.

The integral in (A3) may thus be rewritten as

$$e^{i\mathbf{q}\cdot\mathbf{x}_s(\mathbf{R})} \int \chi_0^2[\mathbf{u}_1 - \mathbf{x}_1(l's'), \dots] e^{i\mathbf{q}\cdot[\mathbf{u}_{ls} - \mathbf{x}_{ls}(l's')]} du, \quad (\text{A5})$$

with $\mathbf{q} = \mathbf{K} - \mathbf{K}'$. χ_0 is the usual oscillator function, but of shifted coordinates.

When the Cartesian coordinates u are transformed into normal coordinates the integral in (A5) becomes a product over all normal coordinates of Fourier transforms of Gaussian functions, which is again a product of Gaussians. The final product turns out to be essentially of the form $\exp(-q^2 \times \text{const})$. For all crystals apt to be of interest it is of order $\exp(-10^{-7})$ for about as large values of q (one over radius of the impurity orbits), as one needs to consider. Accordingly, the product will be replaced by unity, a replacement which, it will be noted becomes exact as q tends to zero. The result is that (A3) becomes

$$\rho_{i0}(\mathbf{K}, \mathbf{K}') = L^{-1} \sum_{l's', \mathbf{R}} Z_s e^{i\mathbf{q}\cdot[\mathbf{x}_s(\mathbf{R}) + \mathbf{R}]}. \quad (\text{A6})$$

For fixed s' , s is determined by \mathbf{R} in (A6).

For about the largest q of interest, $qR' \lesssim 1/10$, where R' is the smallest nonvanishing value of R . This fact will allow one to replace (A6) by integrals. First, one notes that since $\mathbf{x}_s(\mathbf{R}')$ is not more than a few percent of R' , $\mathbf{q}\cdot\mathbf{x}$ is rather a small quantity.

Consequently, one can expand (A6):

$$\rho_{i0} = L^{-1} \sum_{l's', \mathbf{R}} Z_s [\cos \mathbf{q}\cdot\mathbf{R} - \mathbf{q}\cdot\mathbf{x}_s \sin \mathbf{q}\cdot\mathbf{R} - \frac{1}{2}(\mathbf{q}\cdot\mathbf{x}_s)^2 \cos \mathbf{q}\cdot\mathbf{R} + \dots]. \quad (\text{A7})$$

For nonvanishing q the first term in (A7) is zero. The terms of order higher than unity in q can be neglected.

If d is the number of crystal cells per unit volume,

$$\sum_{\mathbf{R}} Z_s \mathbf{q}\cdot\mathbf{x}_s \sin \mathbf{q}\cdot\mathbf{R} \rightarrow d \sum_s \int \mathbf{q}\cdot\mathbf{x}_s(\mathbf{R}) \sin \mathbf{q}\cdot\mathbf{R} d\mathbf{R}, \quad (\text{A8})$$

where the integral is over all of R space, and the summation over all ions s in a crystal cell. The assumption is now made that $\mathbf{x}_s(\mathbf{R})$ is zero up to some radius R_0 , and satisfies (A4) beyond that. (A8) then becomes a straightforward integration, and the total result

becomes independent of s' . Finally, one gets

$$\rho_{i0}(\mathbf{q}) = -4\pi d [\sin qR_0 / (qR_0)] \sum_s Z_s f_s. \quad (\text{A9})$$

In the theory of weak electron-lattice coupling, ($\alpha < 1$), one finds that the ionic polarization surrounding the polaron satisfies the inverse-square law down to radii $\sim 1/K_p$ (see Sec. 3), and gradually dies out for smaller radii.¹⁵ Here one can, therefore, identify R_0 with $1/K_p$. For stronger coupling the inverse square law holds down to even smaller radii.¹³ One can, therefore, say that for all q of interest $qR_0 < 1$. Equation (A9) supports an assumption made in going from (13) to (15) in Sec. 2, namely that $\rho_{i0}(\mathbf{K}, \mathbf{K}', \mathbf{K} - \mathbf{K}')$ is sufficiently slowly varying that it may everywhere be replaced by the limiting value given in (14).

In the limit as q tends to, but does not equal, zero one has

$$\lim_{q \rightarrow 0, q \neq 0} \rho_{i0}(q) = -4\pi d \sum_s Z_s f_s. \quad (\text{A10})$$

This limit is exact, save for overlap terms neglected in deriving (A3). Presumably these can be reduced or eliminated by an appropriate choice of the W_{ls} without rendering (A4) invalid for sufficiently large R .

Consider now the perfect insulating crystal with a fixed extra charge e . At a sufficient distance R from the charge there will be induced, in accordance with (A4), an ionic polarization $\mathbf{P}_i(R)$, which satisfies the equations:

$$\frac{4\pi \mathbf{P}_i(R)}{\mathbf{D}(R)} = \frac{-4\pi e d \sum_s Z_s f_s \mathbf{R} / R^3}{e \mathbf{R} / R^3} = -4\pi d \sum_s Z_s f_s, \quad (\text{A11})$$

where \mathbf{D} is the corresponding displacement field. Finally, from (A10) and (A11) one has the simple result,

$$\lim_{q \rightarrow 0, q \neq 0} \rho_{i0}(\mathbf{q}) = 4\pi \mathbf{P}_i / \mathbf{D}. \quad (\text{A12})$$

By definition,

$$1 - 1/\kappa = 4\pi (\mathbf{P}_i + \mathbf{P}_e) / \mathbf{D}, \quad (\text{A13})$$

where P_e is the "electronic" polarization. Comparison with (12), (14), and (A12) gives

$$(N+1) \lim_{\mathbf{K}, \mathbf{K}' \rightarrow 0; \mathbf{K} \neq \mathbf{K}'} (\Phi_{0\mathbf{K}}^*, \Phi_{0\mathbf{K}'}) = 1 - 4\pi P_e / D. \quad (\text{A14})$$

It is suggestive that one may write the identical equation in the nonpolar problem.^{1,9} There $\Phi_{0\mathbf{K}}, \Phi_{0\mathbf{K}'}$ depend only on electronic coordinates, and there is no ionic polarization P_i additional to P_e .