Pseudopotential Theory of Exciton and Impurity States*

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A formalism for studying central-cell corrections to the effective-mass equation is presented. A generalized impurity equation for excitons and impurity states is derived, including the effects of dielectric response and large-k variation of the effective mass. Because of the presence of interband matrix elements of the impurity potential in the general case, this equation is not easily solved. By transforming to a representation in which the core parts of Bloch functions are removed, a pseudo-wave-equation is developed. In this equation the effective impurity potential is substantially cancelled within the central cell, so that interband matrix elements are sharply reduced, and the usual one-band approximation is valid.

1. INTRODUCTION

OPTICAL absorption spectra of nonmetallic crystals generally contain, in addition to a background of interband scattering structure, a number of well-defined peaks which can be associated with localized states. These states fall into two categories: (1) impurity states,[1] in which an electron or hole is bound to an impurity, and (2) exciton states,[2] in which an electron is bound to a hole in the valence charge distribution. We introduce the binding energy as the energy difference between an appropriate interband threshold and a peak centroid, so that we may further divide our bound states into (a) "shallow" states, characterized by binding energies small compared with a conduction or valence bandwidth, and (b) "deep" states. We have four classes altogether:

(1a) Shallow impurity states, as in n-type or p-type semiconductors; e.g., P in Si, As in Ge, Pb in Ge;

(1b) deep impurity states, located around impurities in insulating crystals; e.g., Xe in Ar, H in Ar;

(2a) shallow excitons, observed in pure semiconductors; e.g., Ge or Si; and

(2b) deep excitons, occurring in filled shell insulators; e.g., Xe, Kr, KBr.

We will show below that there is a generalized impurity equation which may be used to study all of these classes, demonstrating the essential unity of our subject. It has been customary to treat each class separately, owing in part to the fact that the models developed have not been useful for both strong-coupling and weak-coupling problems.

The simplest bound-state model, the Wannier model,[3] is appropriate to the semiconductors, where the impurity or exciton binding energies are small ($\lesssim 0.01$ eV) and the bandwidth large (~ 3 eV). Then because of the large dielectric constant, the Coulomb attraction of the hole or impurity for the excited particle is substantially screened by valence-shell polarization, and we have a weak-coupling situation. If the wavelength of the excited particle is large compared with the lattice parameter, the microscopic variation of the crystal and impurity potentials is "averaged out"; we can replace the impurity potential by a hydrogenic potential embedded in a uniform dielectric. In addition, because of the large bandwidth, the crystal potential can be subsumed into a renormalized mass, or "effective mass" for the band (or bands) of interest. Using this model, also called the effective-mass approximation (EMA), one can reduce the wave equations for excitons or impurity states to a hydrogenic equation[1] for an envelope function. From this result we expect a Rydberg series of energy levels below the interband threshold, with oscillator strengths varying as n^{-3}. The model has been extended by Dresselhaus[4] for excitons and by Kohn and Luttinger[5] for impurity states to include degenerate extrema of the band structure. The EMA has been widely used in the treatment of shallow bound states, for both excitons[6] and impurity states.[1]

A second model, useful in strong-coupling problems, was developed by Frenkel,[7] who was interested in alkali halide spectra. He proposed an interpretation of excitonic states in terms of a Heitler-London model, in which the zero-order charge density of the excited electron is confined to the neighborhood of the lattice site from which it was excited, forming in this manner a state of essentially atomic character. Owing to the translational symmetry of the lattice, this state is degenerate with equivalent states on all other lattice sites; ordinarily a resonance-transfer interaction mixes these into a stationary packet belonging to a wave vector of the Brillouin zone. Similarly, a Frenkel model for a deep impurity state can be imagined, in which the bound particle is confined to the neighborhood of the impurity, so that the wave packet has a wide spread of

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[6] For a good review see T. P. Mc Lean, in *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1961) Vol. 5, p. 55.
[7] J. Frenkel, Phys. Rev. **37**, 17 (1931); **37**, 1276 (1931).

momenta, in accordance with the uncertainty principle. Within the framework of Heitler-London theory, Knox[8] corrected the Frenkel model for the nonorthogonality of atomic functions centered on different sites by Löwdin's technique of symmetric orthogonalization,[9] to second order in overlap integrals. The poor convergence of this method for excited states led Gold[10] to propose that orthogonalization be treated exactly, by the well-known Schmidt procedure. His calculations for a substitutional Ar impurity in solid Ne,[10] and for a hydrogenic impurity in solid Ar,[11] show that exact satisfaction of the orthogonality requirement yields improved agreement with experiment.[12] Overhauser[13] further improved strong-coupling theory by incorporating nearest-neighbor charge-transfer states into the wave function, thereby allowing greater electron-hole separation than in the early Frenkel model.

For many years since the pioneering work of Frenkel and Wannier it was expected that if the shallow bound states were describable by the EMA, then the deep states should be considered from the point of view of the Frenkel model. However, the optical experiments of Baldini[14] on the solid rare gases disclosed the unexpected result that the deep $1s$ excitons in Kr and Xe have energies not far from the EMA predictions obtained by extrapolating the Rydberg series of the shallow excitons for these materials. According to the usual criteria[1] for the validity of the EMA, that interband matrix elements of the impurity potential be negligible, we have the requirement

$$q = (E_G/E_I)(a_0/a) \gg 1. \qquad (1.1)$$

Here E_G and E_I are the values of the energy gap and the binding energy, respectively, while a_0/a is the effective Bohr radius relative to the atomic radius a. In general

$$a_0 = (\hbar^2/me^2)\epsilon_0(m^*/m)^{-1},$$

where ϵ_0 is the macroscopic dielectric constant and m^* is an appropriate effective mass. q is a macroscopic "quality" parameter, being independent of microscopic variations in the crystal or impurity potentials. We define a relative hydrogenic defect d as the central cell correction $E_I - E_0$ relative to E_0, the binding energy in the EMA, that is,

$$d = (E_I - E_0)/E_0.$$

One expects to find small defects for shallow states (large q) and substantial defects for deep states (small q), according to (1.1). Table I lists corresponding q and d values for (A) deep excitons in Kr and Xe, and (B)

[8] R. S. Knox, J. Phys. Chem. Solids **9**, 238 (1959); **9**, 265 (1959).
[9] P. O. Löwdin, Advan. Phys. **5**, 1 (1956).
[10] A. Gold, Phys. Rev. **124**, 1740 (1961).
[11] T. Keil and A. Gold, Phys. Rev. **136**, A252 (1964).
[12] O. Schnepp and K. Dressler, J. Chem. Phys. **33**, 49 (1960); G. Baldini, Phys. Rev. **136**, A248 (1964).
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[14] G. Baldini, Phys. Rev. **128**, 1562 (1962).

TABLE I. Relative hydrogenic defects compared with Kohn's macroscopic quality parameter.

		a_0/a	q	d
(A)	Kr	1.2	8	−0.13[a]
	Xe	1.7	18	0.07[a]
(B)	Ge	16	3200	0.24[b]
	Si	7.4	1000	0.62[b]

[a] Exciton Rydberg series; see Ref. 14.
[b] Averaged over P, As, and Sb donor impurities; see Ref. 1.

shallow impurity states in n-type Ge and Si. Surprisingly, the EMA is more successful for the strong-coupling situation (A) than it is for the weak-coupling case (B) for which it was developed, although the quality differs by factors of order 100.

The failure of the macroscopic criterion (1.1) led us to explore the validity of the EMA from a microscopic viewpoint, taking into account the short-wavelength variations of the periodic and impurity potentials in the analysis. In this paper we report the methods and results of this study. We begin, in Sec. 2, with the formulation of a wave equation appropriate for both excitions and impurity states, and valid in both strong-coupling and weak-coupoing problems. This equation is transformed into a more convenient form in Sec. 3; in this representation interband matrix elements will be shown to be negligible. Within this approximation, the separate contributions to the hydrogenic defect are isolated and identified in Sec. 4. Section 5 contains a discussion of bound-state anomalies, based on the microscopic theory. We conclude that although the Wannier theory works well in case (1a) and badly in (1b), for a wide class of insulators it should work well in both (2a) and (2b), when microscopic corrections are included in the theory.

2. "IMPURITY" EQUATION FOR EXCITONS

The calculation of impurity states is usually based on a one-electron equation

$$[H_0 + U(\mathbf{r} - \mathbf{R}_i)]\psi(\mathbf{r} - \mathbf{R}_i) = E\psi(\mathbf{r} - \mathbf{R}_i), \qquad (2.1)$$

in terms of an unperturbed Hamiltonian

$$H_0 = -(\hbar^2/2m)\nabla^2 + V_0(\mathbf{r})$$

and a screened impurity potential

$$U = V' + V''.$$

Here V_0 is the periodic crystal potential, V' is the "bare" or unscreened impurity potential, and V'' is the polarization potential describing the many-electron response to V'. While V_0 possesses full crystal symmetry, the perturbation U is generally of atomic symmetry, so that $\psi(\mathbf{r} - \mathbf{R}_i)$, the wave function for the impurity state, is a mixture of Bloch states for the conduction bands

$$\psi(\mathbf{r} - \mathbf{R}_i) = \sum_{n\mathbf{k}} g_n(\mathbf{k})\varphi_{n\mathbf{k}}(\mathbf{r} - \mathbf{R}_i). \qquad (2.2)$$

The $\varphi_{n\mathbf{k}}$ are chosen to satisfy

$$H_0\varphi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_n(\mathbf{k})\varphi_{n\mathbf{k}}(\mathbf{r}).$$

Because U is a localized potential it is formally convenient to expand ψ in terms of Wannier functions;

$$a_{n\mathbf{R}}(\mathbf{r}) = N^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}}\varphi_{n\mathbf{k}}(\mathbf{r}), \qquad (2.3)$$

where N is the number of primitive cells in the crystal, and the k-space sum is restricted to the first Brillouin zone. It is known[15] that $a_{n\mathbf{R}}$ is localized around lattice site $\mathbf{R}$ with an average radius approximately equal to a lattice parameter. In terms of the $a_{n\mathbf{R}}$,

$$\psi(\mathbf{r}-\mathbf{R}_i) = \sum_{n\mathbf{R}} f_n(\mathbf{R})a_{n\mathbf{R}}(\mathbf{r}-\mathbf{R}_i). \qquad (2.4)$$

According to (2.3) we have

$$f_n(\mathbf{R}) = N^{-1/2}\sum_{\mathbf{k}} g_n(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}}.$$

In the Wannier representation, we have, instead of (2.1),

$$\sum_{n'\mathbf{R}'} [W_n(\mathbf{R}-\mathbf{R}')\delta_{nn'} + U_{nn'}(\mathbf{R},\mathbf{R}')]f_{n'}(\mathbf{R}')$$
$$= Ef_n(\mathbf{R}), \qquad (2.5)$$

where

$$W_n(\mathbf{R}-\mathbf{R}') = N^{-1}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')}\epsilon_n(\mathbf{k}),$$

and

$$U_{nn'}(\mathbf{R},\mathbf{R}') = \int d\mathbf{r}\, a_{n\mathbf{R}}^*(\mathbf{r})U a_{n'\mathbf{R}'}(\mathbf{r}).$$

In this equation the periodic potential is assimilated into a "kinetic-energy term" W_n, while $U_{nn'}$, the "potential-energy term," contains the effect of the impurity potential. In strong-coupling problems the impurity state may be so localized that many conduction bands will contribute to the wave packet. Then the expansions (2.2) and (2.4) may not be convenient; in this case an expansion in terms of Heitler-London atomic orbitals is more appropriate. This is generally true of the deep impurity states in molecular crystals.

Here we show that excitonic states satisfy an equation like (2.1); this will be useful in the general discussion below. We begin with a brief review of exciton theory,[2] keeping the discussion general so as to include both strong- and weak-coupling limits. The discussion is restricted to "direct" formation of excitons, i.e., optical transitions unaccompanied by phonon absorption or emission. Then the center-of-mass momentum of the exciton must be equal to the photon momentum, which is negligibly small compared to characteristic electron momenta. In addition, since electric dipole transitions are allowed for all cases of interest, we need consider only singlet spin states $(S=0)$.

The space part of an excitonic state is usually represented as a superposition of electron-hole scattered pairs, bound by the residual Coulomb attraction into a localized packet with energy less than that of the uncorrelated pairs. Following Slater and Shockley,[16] we introduce an "exciton representation" for the wave packet; each basis function is an eigenfunction of crystal momentum constructed from a single pair of bands. For an electron in band n and a hole in band m we have

$$\chi_{mn}(\mathbf{K},\boldsymbol{\beta}) = N^{-1/2}\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\boldsymbol{\beta}}B_{mN}(\mathbf{k},\mathbf{k}+\mathbf{K}), \qquad (2.6)$$

where $\boldsymbol{\beta}$ is a lattice vector and B_{mn} is a Slater determinant of Bloch functions given by

$$B_{mn}(\mathbf{k},\mathbf{k}+\mathbf{K}) = A\{\varphi_{m\mathbf{k}_1}(\mathbf{r}_1)\cdots\varphi_{m\mathbf{k}_N}(\mathbf{r}_N)$$
$$\times[\varphi_{m\mathbf{k}}(\mathbf{r}_h)\varphi_{n\ \mathbf{k}+\mathbf{K}}(\mathbf{r}_e)]\}.$$

A is the antisymmetrization operator; r_e and r_h refer to electron and hole coordinates, respectively; B_{mn} is an $(N+2)$-particle wave function for a full valence band augmented by a Bloch electron-hole pair of momentum $\mathbf{K}$. In terms of Wannier functions, (2.6) can be written as

$$\chi_{mn}(\mathbf{K},\boldsymbol{\beta}) = N^{-1/2}\sum_{\mathbf{R}} e^{i\mathbf{K}\cdot\mathbf{R}}W_{mn}(\mathbf{R},\mathbf{R}+\boldsymbol{\beta}), \qquad (2.7)$$

using (2.3), where W_{mn} is the wave function for a full valence band to which has been added a Wannier electron-hole pair of separation $\boldsymbol{\beta}$:

$$W_{mn}(\mathbf{R},\mathbf{R}+\boldsymbol{\beta}) = A\{a_{m R_1}(\mathbf{r}_1)\cdots a_{m R_N}(\mathbf{r}_N)$$
$$\times[a_{m\mathbf{R}}(\mathbf{r}_h)a_{n\ \mathbf{R}+\beta}(\mathbf{r}_e)]\}.$$

Expressions (2.6) and (2.7) illustrate the formal equivalence of real-space and momentum-space pictures of the exciton; each basis function ψ has associated with it a crystal momentum $\mathbf{K}$ for the center-of-mass motion and a lattice vector $\boldsymbol{\beta}$ for the electron-hole separation. In the exciton representation one expands the excitonic state in terms of these functions; i.e., for the νth exciton of momentum $\mathbf{K}$,

$$\Psi^{\nu\mathbf{K}} = \sum_{mn\beta} F_{mn}{}^{\nu\mathbf{K}}(\boldsymbol{\beta})\chi_{mn}(\mathbf{K},\boldsymbol{\beta}). \qquad (2.8)$$

Exciton eigenvalues $E_{\nu\mathbf{K}}$ are determined along with the eigenvectors $F_{mn}(\boldsymbol{\beta})$ by solving the Schrödinger equation

$$H\Psi^{\nu\mathbf{K}} = E_{\nu\mathbf{K}}\Psi^{\nu\mathbf{K}}, \qquad (2.9)$$

where H is the N-particle Hamiltonian

$$H = \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\nabla_i{}^2 + U_0(\mathbf{r}_i)\right] + \tfrac{1}{2}\sum_{i\neq j}\frac{e^2}{r_{ij}}; \qquad (2.10)$$

the first term is the total-kinetic-energy operator, U_0 is the ionic potential, and the last term is the Coulomb

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[16] J. C. Slater and W. Shockley, Phys. Rev. 50, 705 (1936).

interaction. On substituting (2.8) into (2.9), we get

$$\sum_{m'n'\beta'} \langle mn\mathbf{K}\beta | H | m'n'\mathbf{K}\beta' \rangle F_{m'n'}{}^{\nu\mathbf{K}}(\beta')$$
$$= E_{\nu\mathbf{K}} F_{mn}{}^{\nu\mathbf{K}}(\beta), \quad (2.11)$$

a set of coupled algebraic equations for the F_{mn}, where

$$\langle mn\mathbf{K}\beta | H | m'n'\mathbf{K}\beta' \rangle = \int d\tau \, \chi_{mn}{}^*(\mathbf{K}\beta) H \chi_{m'n'}(\mathbf{K}\beta');$$

the integration extends over the coordinates of $(N+2)$ particles. For most cases of interest we may neglect matrix elements between the more localized hole bands, although interband mixing of delocalized electron states is often essential in this representation. Suppressing $m=m'$, $\mathbf{K}(K=0)$, and ν, and subtracting the ground-state energy from the diagonal, we have

$$\sum_{n'\beta'} H_{nn'}(\beta\beta') F_{n'}(\beta') = EF_n(\beta), \quad (2.12)$$

where

$$H_{nn'}(\beta\beta') = N^{-1} \sum_{\mathbf{k}} \exp[i\mathbf{k}\cdot(\beta-\beta')]$$
$$\times [\epsilon_n(\mathbf{k}) - \epsilon_m(\mathbf{k})]\delta_{nn'}$$
$$+ \sum_{\mathbf{R}} [2\langle n\beta m\mathbf{R} | g^0 | m0n'\mathbf{R}+\beta' \rangle$$
$$- \langle n\beta m\mathbf{R} | g^0 | n'\mathbf{R}+\beta'm0 \rangle]. \quad (2.13)$$

Here ϵ_n and $(-\epsilon_m)$ are Hartree-Fock energies for a "conduction" electron and a "valence" hole, respectively. Thus

$$\omega_n(\mathbf{k}) = \epsilon_n(\mathbf{k}) - \epsilon_m(\mathbf{k})$$

is the energy of an electron-hole pair before correlation due to their Coulomb attraction is added. The correlation terms are given by the lattice sum in (2.13), in which

$$g^0 = e^2 / |\mathbf{r}_e - \mathbf{r}_h|, \quad (2.14)$$
and

$$\langle n\beta m\beta' | g_0 | n'\beta''m\beta''' \rangle$$
$$= \int d\mathbf{r}_e d\mathbf{r}_h a_{n\beta}{}^*(\mathbf{r}_e) a_{m\beta'}{}^*(\mathbf{r}_h) g^0 a_{n'\beta''}(\mathbf{r}_e) a_{m\beta'''}(\mathbf{r}_h).$$

The first term in the square brackets in (2.13) is an exchange interaction between the electron and hole, while the direct Coulomb interaction is given in the second term. Terms for $\mathbf{R}\neq0$ are often called excitation transfer matrix elements and are negligibly small unless the valence bandwidth is large. We introduce a one-electron potential derived from the interaction terms of (2.13); i.e.,

$$v(\mathbf{r}) = v_D(\mathbf{r}) + v_x(\mathbf{r}) \quad (2.15)$$

in terms of a direct Coulomb interaction v_D, given by

$$v_D\psi(\mathbf{r}) = -\sum_{\mathbf{R}} \left\{ \left[\int d\mathbf{r}' a_{m\mathbf{R}}{}^*(\mathbf{r}') g^0(\mathbf{r}-\mathbf{r}') a_{m0}(\mathbf{r}') \right] T_{\mathbf{R}}\psi(\mathbf{r}) \right\}$$

for an arbitrary function $\psi(\mathbf{r})$, and an exchange interaction v_x, given by

$$v_x\psi(\mathbf{r}) = 2\sum_{\mathbf{R}} \left\{ \left[\int d\mathbf{r}' a_{m\mathbf{R}}{}^*(\mathbf{r}') g^0(\mathbf{r}-\mathbf{r}') T_{\mathbf{R}}\psi(\mathbf{r}') \right] a_{m0}(\mathbf{r}) \right\},$$
where

$$T_{\mathbf{R}}\psi(\mathbf{r}) = \psi(\mathbf{r}-\mathbf{R}).$$

In addition, we introduce an auxiliary one-electron function

$$\psi(\mathbf{r}) = \sum_{n\beta} G_n(\beta) a_{n\beta}(\mathbf{r}), \quad (2.16)$$

which should be compared with

$$\Psi = \sum_{n\beta} F_n(\beta) \chi_{mn}(0,\beta),$$

the $(N+2)$-particle wave function for an excitonic state of the crystal. We will show that ψ satisfies a one-electron Schrödinger equation

$$(h_0+v)\psi = \epsilon\psi, \quad (2.17)$$

provided we choose $G_n=F_n$ and $\epsilon=E$, the exciton energy relative to the ground state. Here

$$h_0 = H_0 - W,$$

where H_0 is the one-electron Hamiltonian for the perfect crystal:

$$H_0\varphi_{n\mathbf{k}} = \epsilon_n(\mathbf{k})\phi_{n\mathbf{k}},$$

as before, and W is an operator defined by

$$W\varphi_{n\mathbf{k}} = -\epsilon_m(\mathbf{k})\varphi_{n\mathbf{k}}.$$

Then we have, using (2.3),

$$\langle n\beta | h_0 | n'\beta' \rangle = N^{-1} \sum_{\mathbf{k}} \exp[i\mathbf{k}\cdot(\beta-\beta')]$$
$$\times [\epsilon_n(\mathbf{k}) - \epsilon_m(\mathbf{k})]\delta_{nn'}. \quad (2.18)$$

Taking matrix elements of v_D and v_x, we have also

$$\langle n\beta | v | n'\beta' \rangle = \sum_{\mathbf{R}} [2\langle n\beta m\mathbf{R} | g^0 | m0n'\mathbf{R}+\beta' \rangle$$
$$- \langle n\beta m\mathbf{R} | g^0 | n'\mathbf{R}+\beta'm0 \rangle]. \quad (2.19)$$

Substituting (2.16) into (2.17) we have

$$\sum_{n'\beta'} [\langle n\beta | h_0 | n'\beta' \rangle + \langle n\beta | v | n'\beta' \rangle] G_{n'}(\beta') = \epsilon G_n(\beta).$$

From (2.18), (2.19), and (2.12), we see that this set of equations is identically satisfied if $G_n=F_n$ and $\epsilon=E$; with these choices, ψ satisfies (2.17) and has the exciton eigenvalue E. The wave function Ψ for the exciton state can also be determined from the solution of (2.17), for

$$F_n(\beta) = \int d\mathbf{r} \, a_{n\beta}{}^*(\mathbf{r})\psi(\mathbf{r}).$$

Thus, we have replaced the $(N+2)$-particle problem with a one-electron impurity problem, Eq. (2.17), for

$h_0(\mathbf{r})$ has the full lattice symmetry and is known if the band structure is known, while v is a symmetry-breaking interaction, localized about $\mathbf{R}=0$. For electron-hole separations large compared to an atomic radius, we expect v to be hydrogenic; the exchange terms are negligible in this case, while Gauss' theorem applied to the Coulomb integral gives $v_D(\mathbf{r}) \propto |\mathbf{r}|^{-1}$. In any case, Eq. (2.17) is conceptually simpler than (2.12) and the same form as (2.1), so that both excitons and impurity states may be studied from the same viewpoint, which is the result we sought to derive.

Before we treat the general problem we point out a serious defect of the exciton representation (2.8) for low-lying excited states of the crystal. The restriction to two-particle excitations is not exact, inasmuch as the valence charge density is strongly perturbed by the multipole field of the pair. Thus, the charge distribution in the neighborhood of the electron-hole pair will be polarized, setting up an electrostatic potential which opposes the multipole field of the pair and reduces the electron-hole interaction. In order to calculate better eigenstates of this system we ought to include multiple-exciton states, compute matrix elements between them, and diagonalize this much larger matrix. The treatment of this problem belongs to many-body theory, and will be summarized in Sec. 4. Here it is sufficient to represent the polarization effects by a self-consistent potential for the electron-hole coupling,

$$u = v + p(u).$$

Thus the bare electron-hole interaction v is screened by a polarization potential p, which represents the self-consistent response of the valence charge distribution to the excited pair. Then Eq. (2.17) is replaced by

$$(h_0 + u)\psi = E\psi. \qquad (2.20)$$

3. IMPURITY CANCELLATION THEORY

Let us consider Eqs. (2.1) and (2.20) to be special cases of a generalized impurity equation

$$[K_0 + V'(\mathbf{r} - \mathbf{R}_i)]\psi(\mathbf{r} - \mathbf{R}_i) = E\psi(\mathbf{r} - \mathbf{R}_i) \qquad (3.1)$$

in which the positive charge is centered at $\mathbf{R}_i$,

$$K_0 = -(\hbar^2/2m)\nabla^2 + V^0(\mathbf{r})$$

has full crystal symmetry, and $V'(\mathbf{r} - \mathbf{R}_i)$ is the "impurity" potential. In general, this equation is extremely difficult to solve because of the crossed symmetries of V^0 and V'. However, if V' is strong enough to confine ψ to the vicinity of the central cell, it may be possible to treat V^0 as a perturbation from nearest neighbors (Heitler-London model). On the other hand the impurity potential may be so weak that a characteristic wavelength of ψ is large compared with an atomic radius, so that the microscopic details of V^0 and V' are unimportant and the EMA is valid [see Eq. (1.1)]. In the general case neither approach is valid, and expansions (2.2) and (2.4) are not rapidly convergent. In the Wannier representation we have

$$\sum_{n'\mathbf{R}'} [W_n(\mathbf{R} - \mathbf{R}')\delta_{nn'} + V_{nn'}'(\mathbf{R}\mathbf{R}')]F_{n'}(\mathbf{R}')$$
$$= EF_n(\mathbf{R}), \qquad (3.2)$$

where

$$W_n(\mathbf{R} - \mathbf{R}') = N^{-1} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} \epsilon_n(\mathbf{k})$$

and

$$V_{nn'}'(\mathbf{R}\mathbf{R}') = \int d\mathbf{r} \, a_{n\mathbf{R}}^*(\mathbf{r}) V' a_{n'\mathbf{R}'}(\mathbf{r}).$$

If V' were slowly varying compared to the lattice parameter, the orthogonality properties of the Wannier functions would imply

$$V_{nn'}'(\mathbf{R}\mathbf{R}') = \delta_{nn'}\delta_{\mathbf{R}\mathbf{R}'}V_n'(\mathbf{R}), \qquad (3.3)$$

where

$$V_n'(\mathbf{R}) = V_{nn}'(\mathbf{R}\mathbf{R}).$$

Blount has shown[17] that if (3.3) holds, then (3.2) can be transformed into a differential equation

$$[\epsilon_n(-i\nabla) + V_n'(\mathbf{r})]f_n(\mathbf{r}) = Ef_n(\mathbf{r}), \qquad (3.4)$$

where ϵ_n satisfies

$$K_0\varphi_{n\mathbf{k}} = \epsilon_n(\mathbf{k})\varphi_{n\mathbf{k}}$$

and

$$V_n'(\mathbf{r}) \equiv \sum_{\mathbf{R}} \int d\mathbf{k} \, V_n'(\mathbf{R}) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}.$$

f_n is a continuous function in real space, related to F_n by

$$f_n(\mathbf{R}) = F_n(\mathbf{R}).$$

Equation (3.4) is especially useful for large-radius states, for then only a small volume of k-space contributes to the wave packet ψ, and $\epsilon_n(\mathbf{k})$ for this region may be approximated by a quadratic form. We point out that small-radius states may be studied conveniently with the algebraic equations (3.2), provided that $\epsilon_n(\mathbf{k})$ is known and (3.3) holds. For these states only a small set of Wannier functions will be important, and the energy may be determined by solving the secular equation

$$\det|W_n(\mathbf{R} - \mathbf{R}') + [V_n'(\mathbf{R}) - E]\delta_{\mathbf{R}\mathbf{R}'}| = 0. \qquad (3.5)$$

Thus impurity states in any category are amenable to calculation, using either (3.4) or (3.5), only if interband matrix elements $V_{mn'}'$ may be ignored as in (3.3).

For a screened hydrogenic potential $V_n'(\mathbf{r}) \propto r^{-1}$ and for parabolic conduction bands, (3.3) will not be valid when $a_0/a \lesssim 2$ or 3 because of the strength of V' at small r (central atomic cell). Because we are interested in deep states as well as shallow states we must find a way of removing the strong "core part" of V from the general problem (3.1). Let us recall how this was done for another problem.

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[17] E. I. Blount, Solid State Phys. 13, 305 (1962).

In determining the Bloch functions ψ_k it is convenient to expand each state in plane waves. However, because the one-electron potential V_0 is strong and rapidly varying in the core regions, a Fourier expansion converges slowly. Herring[18] showed that rapid convergence could be obtained by orthogonalizing the plane waves to core orbitals. Mixing of orthogonalized plane-wave basis states is greatly reduced because of the substantial cancellations between matrix elements of the core potential and core orthogonality terms. The latter are rigorously equivalent to a nonlocal energy-dependent potential, but Phillips and Kleinman[19] argued that for many practical purposes they could be replaced by an ordinary repulsive potential $V_R(\mathbf{r})$. The cancellation between V_0 and V_R in the core region was then manifest, and one obtained a wave equation for the "smooth" part ϕ_k of ψ_k given by

$$(T+V_0+V_{0R})\phi_k=E\phi_k, \qquad (3.6)$$

in which V_{0R} opposes V_0 in the core region and T is the kinetic-energy operator. The form of V_{0R} depends on the specification of ϕ_k in terms of the true wave function

$$\psi_k=\phi_k-\sum_t \langle\phi_t|\phi_k\rangle\phi_t, \qquad (3.7)$$

where the ϕ_t are core functions. Cohen and Heine chose the smoothest (smallest interband mixing) compatible with (3.6) and (3.7) and obtained the relation

$$V_{0R}\phi_k=-\sum_t \langle\phi_t|V_0|\phi_k\rangle\phi_t, \qquad (3.8)$$

which explicitly exhibits V_R as a projection of V_0 on core states. For large cores cancellation of V_0 by V_{0R} is nearly exact within the core region, as long as ϕ_k has predominantly s or p character. Then the residual pseudopotential

$$V_{\text{ps}}=V_0+V_{0R} \qquad (3.9)$$

is smooth and slowly varying, so that ϕ_k may be represented by a minimal number of plane waves.

Although cancellation theory has previously been considered for periodic structures, it is easy to extend the formalism to include the impurity problem (3.1). We show that transformation to a smooth representation yields an impurity pseudopotential that is weak in the core regions, with the important result that interband matrix elements of the central cell potential are substantially reduced. We will find, as before, that there is a pseudopotential associated with the perfect crystal as well. Because of the manifest cancellation of the impurity potential one can now justify (rather than assume *ad hoc*) the validity of a one-band model for deep as well as shallow exciton states.

Following Phillips and Kleinman, we represent $\psi(\mathbf{r}-\mathbf{R}_i)$ as the sum of a smooth function and its

Schmidt corrections

$$\psi(\mathbf{r}-\mathbf{R}_i)=\phi(\mathbf{r}-\mathbf{R}_i)-\sum_m \langle\phi_m|\phi\rangle\phi_m, \qquad (3.10)$$

where the ϕ_m are core functions in the presence of the impurity, and are different functions in different cells, in general. For strong coupling problems the calculation of the ϕ_m may be itself a difficult problem. We substitute (3.10) into (3.1) to get

$$[T+V^0(\mathbf{r})+V'(\mathbf{r}-\mathbf{R}_i)+V_R]\phi(\mathbf{r}-\mathbf{R}_i)$$
$$=E\phi(\mathbf{r}-\mathbf{R}_i), \qquad (3.11)$$

an effective wave equation for ϕ, where

$$V_R\phi=\sum_m (E-E_m)\langle\phi_m|\phi\rangle\phi_m; \qquad (3.12)$$

E_m denotes the energy of the mth core level. Following Cohen and Heine[20] we exploit the fact that variations in ϕ of the type

$$\delta\phi=\sum_m \alpha_m\phi_m$$

produce no change in ψ. We seek α_m that will minimize the potential energy of ϕ,

$$F(\phi)=\langle\phi|V^0+V'+V_R|\phi\rangle/\langle\phi|\phi\rangle.$$

Since the α_m are independent constants

$$\langle\phi_m|V^0+V'+V_R|\phi\rangle=\frac{\langle\phi_m|\phi\rangle}{\langle\phi|\phi\rangle}$$
$$\times\langle\phi|V^0+V'+V_R|\phi\rangle. \qquad (3.13)$$

According to (3.12) we have

$$\langle\phi_m|V_R|\phi\rangle=(E-E_m)\langle\phi_m|\phi\rangle. \qquad (3.14)$$

Neglecting normalization corrections to ϕ and using (3.13) and (3.14), we find the important result

$$V_R\phi=-\sum_m \langle\phi_m|V^0+V'|\phi\rangle\phi_m. \qquad (3.15)$$

We decompose V_R into a term V_R^0 arising solely from the periodic potential and a term V_R' arising from the impurity potential alone:

$$V_R=V_R^0+V_R', \qquad (3.16)$$

where

$$V_R^0\phi=-\sum_m \langle\phi_m|V^0|\phi\rangle\phi_m,$$

$$V_R'\phi=-\sum_m \langle\phi_m|V'|\phi\rangle\phi_m.$$

From the rigorous analysis of Austin, Heine, and Sham[21] it is easy to see that Eq. (3.16) is exact in that (3.11) then has the same eigenvalues as (3.1). We can see also

[18] C. Herring, Phys. Rev. **57**, 1169 (1940).
[19] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).
[20] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).
[21] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

that this choice yields a ϕ which is "almost" the smoothest possible for our problem. To see how smooth ϕ may be, we calculate the impurity pseudopotential

$$V_{\rm ps}'(\phi) \equiv \frac{(V'+V_R')\phi}{\phi} = \int d\mathbf{r}' V'(\mathbf{r}')[\delta(\mathbf{r}-\mathbf{r}')$$
$$-\sum_m \phi_m{}^*(\mathbf{r}')\phi_m(\mathbf{r})]\phi(\mathbf{r}')\phi^{-1}(\mathbf{r}), \quad (3.17)$$

while for the crystal potential

$$V_{\rm ps}{}^0(\phi) = \frac{(V^0+V_R{}^0)\phi}{\phi} = \int d\mathbf{r}' V^0(\mathbf{r}')[\delta(\mathbf{r}-\mathbf{r}')$$
$$-\sum_m \phi_m{}^*(\mathbf{r}')\phi_m(\mathbf{r})]\phi(\mathbf{r}')\phi^{-1}(\mathbf{r}).$$

These equations exhibit the cancellation we expected; both V^0 and V' are cancelled as effectively as possible by a linear combination of core states. Thus both potentials are substantially cancelled in the core regions, but are virtually undiminished in the region between cores. The pseudowave equation is, of course,

$$[T+V_{\rm ps}{}^0(\mathbf{r})+V_{\rm ps}'(\mathbf{r}-\mathbf{R}_i)]\phi(\mathbf{r}-\mathbf{R}_i)$$
$$= E\phi(\mathbf{r}-\mathbf{R}_i). \quad (3.18)$$

We show in the Appendix that $V_{\rm ps}{}^0$ has only small terms that break the crystal symmetry; these terms may be absorbed into $V_{\rm ps}'(\mathbf{r}-\mathbf{R}_i)$.

We must now consider under what circumstances the model impurity wave functions $\phi(\mathbf{r}-\mathbf{R}_i)$ can be represented as a wave packet of model states $\phi_{\mathbf{k}}(\mathbf{r})$ derived from Bloch states $\psi_{\mathbf{k}n}$ near a specific band edge $\mathbf{k}=\mathbf{k}_\alpha$. In many insulators the state at the bottom of the conduction band is at $\mathbf{k}=0$ and has Γ_1 symmetry. Because the model wave function $\phi_0(\mathbf{r})$ for Γ_1 is almost constant, we may then use a one-band approximation for $\phi(\mathbf{r}-\mathbf{R}_i)$, even though an expansion of $\psi(\mathbf{r}-\mathbf{R}_i)$ in terms of Bloch states near Γ may contain states from higher bands. Then the effective Hamiltonian approach is tractable: the solutions of the periodic potential problem

$$[T+V_{\rm ps}{}^0(\mathbf{r})]\varphi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_n(\mathbf{k})\varphi_{n\mathbf{k}}(\mathbf{r})$$

are used to cast (3.18) into the form

$$\sum_{\mathbf{R}'}[W_n(\mathbf{R}-\mathbf{R}')+U_{nn'}(\mathbf{R}\mathbf{R}')]f(\mathbf{R}') = Ef(\mathbf{R}). \quad (3.19)$$

Here

$$U_{nn'}(\mathbf{R}\mathbf{R}') = \langle n\mathbf{R}|V_{\rm ps}'|n'\mathbf{R}'\rangle,$$

and f is the envelope function for $\phi(\mathbf{r}-\mathbf{R}_i)$ in the Wannier representation, given by

$$\phi(\mathbf{r}) = \sum_{\mathbf{R}} f(\mathbf{R})\alpha_{n\mathbf{R}}(\mathbf{r}),$$

where $\alpha_{n\mathbf{R}}$ is the smooth part of $\alpha_{n\mathbf{R}}$; i.e.,

$$\alpha_{n\mathbf{R}}(\mathbf{r}) = N^{-1/2} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}}\varphi_{n\mathbf{k}}(\mathbf{r}).$$

Except in extreme strong-coupling situations, when $U_{nn'} \neq 0$ for $n \neq n'$ and (3.18) must be used, (3.19) are the fundamental equations for calculating excitons and impurity states.

The extent to which the foregoing arguments are applicable when the band edge does not have Γ_1 symmetry requires a separate investigation for each case. We may note, however, that the nearly complete cancellation of core and repulsive potentials implies a nearly free electron band structure, with conduction band minimum at Γ_1. Conversely, if the minimum is not at Γ_1, then cancellation cannot be so complete, and large central cell corrections to the hydrogenic model are expected.

4. SCREENED IMPURITY POTENTIAL

In the presence of a localized positive charge the valence charge distribution is polarized to screen the impurity potential. If the Fourier transform of the bare potential is represented by $V'(\mathbf{k})$, the screened potential neglecting local field corrections is given by[22,23]

$$V_s'(\mathbf{r}-\mathbf{R}_i) = \int d\mathbf{k}\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_i)}V'(\mathbf{k})\frac{1}{\epsilon(\mathbf{k},\mathbf{K}=0)}. \quad (4.1)$$

This choice of the screened potential has the convenient asymptotic feature that $V_s' \to (\epsilon_0|\mathbf{r}-\mathbf{R}_i|)^{-1}$ as $|\mathbf{r}-\mathbf{R}_i| \to \infty$, where ϵ_0 is the macroscopic dielectric constant. This is the correct result, as one can show from macroscopic considerations.[24] Within the central cell (4.1) provides a convenient prescription for treating polarization effects. The customary approximation[25,26] made in (4.1) of neglecting local fields retains only the $K=0$ component, because outside the central cell the $K \neq 0$ terms appear to be small.[27] Then from (4.1) we can write

$$V_s'(\mathbf{r}-\mathbf{R}_i) = e^2/\epsilon(\mathbf{r}-\mathbf{R}_i)|\mathbf{r}-\mathbf{R}_i|, \quad (4.2)$$

where the position-dependent screening factor is defined as

$$\epsilon^{-1}(r) = 4\pi r \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{r}}/k^2\epsilon(\mathbf{k},0). \quad (4.3)$$

In practice (4.3) should be regarded as a convenient interpolation formula between the limits $\epsilon = \epsilon_0$ $(r \to \infty)$ and $\epsilon = 1$ $(r \to 0)$.

In the preceding section we showed that, if we choose to work in a representation where the one-band approxi-

[22] M. Azuma, J. Phys. Soc. Japan **18**, 194 (1963).
[23] N. Wiser, Phys. Rev. **129**, 62 (1963).
[24] W. Kohn, Phys. Rev. **110**, 857 (1958).
[25] M. H. Cohen, Phil. Mag. **3**, 762 (1958).
[26] M. A. Biondi and J. A. Rayne, Phys. Rev. **115**, 1522 (1959).
[27] H. Nara, J. Phys. Soc. Japan **20**, 778 (1965).

mation is valid, then polarization of large valence cores has a drastic effect on $V'(\mathbf{r}-\mathbf{R}_i)$ in the central cell. Because of central-cell polarization this is not the Bloch representation, but a modified model representation in which the smooth basis states ϕ have been orthogonalized to polarized core states. In this representation, the effect of central-cell polarization appears as a repulsive potential. Like the polarization potential outside the central cell, the repulsive potential also acts to reduce V'.

The origin of the two screening effects is, however, formally different. The conventional dielectric screening described by (4.3) represents the effect of valence polarization on the interaction between two test charges, with the positions of the latter averaged over an atomic cell [only the $\mathbf{K}=0$ component is retained in (4.1)]. The repulsive potential is in a sense fictitious, because it arises through a special choice of representation suited to minimizing the effects of interband matrix elements of the potential, thus enabling us to make the one-band approximation. (Compare this situation with Schrödinger or Heisenberg representations, the latter being adopted to remove part of the potential from the wave equation.) From another viewpoint, however, the repulsive terms also represent a polarization response to the presence of the positive charge, because they arise from changes in core levels induced by the additional charge.

The unphysical character of the repulsive polarization potential becomes apparent if we assume perfect cancellation between V' and V_R' in the core region $r \lesssim r_c$, and represent the effect of V_R' by a screening factor $\epsilon_R(r)$. This factor then has the property that for $r \lesssim r_c$, $\epsilon_R(r) \to \infty$, rather than 1, as is the case for (4.3). This surprising behavior is implicit in the one-band approximation itself.

5. EXCITON AND IMPURITY STATES

The procedure that has been developed in the preceding sections for constructing local pseudopotentials is applied in the following paper to the calculation of hydrogenic defects of deep exciton and impurity levels in rare-gas crystals. The great success of the Wannier model, which as we saw in Sec. 1 is quite surprising in terms of the macroscopic quantities contained in Eq. (1.1), is seen to follow from the cancellation effects inherent in the pseudopotential approach.

Application of the pseudopotential method to rare-gas crystals is facilitated by the fact that the valence states form closed shells so that the repulsive potential is isotropic in the central cell. Also the situation in the conduction band is favorable because $\phi(\Gamma_1)$ is almost constant over the atomic cell. By contrast, in semiconductors such as Ge the valence shells are only half-filled; and as a consequence, the repulsive potential is concentrated along bonding directions. (The angular variation of the repulsive potential closely resembles

that of the valence charge density, which is strongly anisotropic, being large along bonding directions and falling almost to zero along the antibonding directions.[28,29]) Moreover, $\phi(L_1)$ in Ge varies rapidly over the unit cell, so that different regions of the central cell must be given unequal weights in calculating the expectation values of the $1s$ donor energies. In spite of these essentially geometric complexities we expect that by including cancellation effects in a local pseudopotential representation one should be able to account semiquantitatively for the trends of hydrogenic defects of group-V donor impurity states in Ge and in Si.

In summary, the new feature which distinguishes the present approach from previous ones[1,2] is emphasis on the difference between the microscopic shell structures of the atom occupying the central cell and the atoms composing the host lattice. We retain the Wannier picture based on macroscopic screening of the attractive potential and a one-band kinetic energy outside the central cell. We also retain interpolation within the central cell to include the effects of breakdown of dielectric screening.[1] But we find that to understand even qualitatively the observed variations of hydrogenic defects it is necessary to include the effects of orthogonalization of conduction states to valence shells, especially in the central cell. In the sense discussed in Sec. 4 our model still retains a degree of semiclassical simplicity, but one is now able to understand the large variations of hydrogenic defects which had previously appeared to undermine the utility of the Wannier picture iteself.

APPENDIX: PSEUDOPOTENTIAL SYMMETRIES

In the pure crystal only V_R can break the lattice symmetry in the pseudowave equation

$$(T+V^0+V_R^0)\phi\ (\mathbf{r})=E\phi\ (\mathbf{r}). \tag{A1}$$

But, by (3.8)

$$V_R^0=-\sum_t \frac{\phi_t(\mathbf{r})}{\phi_\mathbf{k}(\mathbf{r})}\int d\mathbf{r}'\phi_t^*(\mathbf{r}')V^0(\mathbf{r}')\phi_\mathbf{k}(\mathbf{r}'). \tag{A2}$$

Since both ϕ_t and $\phi_\mathbf{k}$ are eigenfunctions of crystal momentum [see (3.7)], we may apply the Bloch theorem in the form

$$\begin{aligned}\phi_t(\mathbf{r})&=e^{i\mathbf{k}_t\cdot\mathbf{r}}u_{ck_t}(\mathbf{r}),\\ \phi_\mathbf{k}(\mathbf{r})&=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}),\end{aligned} \tag{A3}$$

where c denotes a "core band" and n is a conduction-band index. The u's have full lattice symmetry. Then

$$\langle\phi_t|\,V^0\,|\phi_\mathbf{k}\rangle=\delta(\mathbf{k}-\mathbf{k}_t)V_{cn}^0(\mathbf{k}), \tag{A4}$$

where

$$V_{cn}^0(\mathbf{k})=\langle u_{c\mathbf{k}}|\,V^0\,|u_{n\mathbf{k}}\rangle. \tag{A5}$$

[28] K. H. Bennemann, Phys. Rev. **133**, A1045 (1964).
[29] L. Kleinman and J. C. Phillips, Phys. Rev. **116**, 880 (1959); **117**, 460 (1960); **118**, 1153 (1960).

Inserting (A4) into (A2) we get

$$V_R{}^0 = -\sum_c \frac{u_{ck}(\mathbf{r})}{u_{nk}(\mathbf{r})} V_{cn}{}^0(\mathbf{k}), \qquad (A6)$$

which has the symmetry of the lattice.

In the impurity problem (3.18) the core states ϕ_t are not eigenfunctions of crystal momentum and (A6) does not hold. On the other hand, it is easy to see that the ϕ_t differ from the pure-crystal functions (A3) only in the neighborhood of V'. Thus, terms in $V_R{}^0$ which do not have full symmetry are localized around the impurity and may be absorbed into the definition of V_{ps}', so that $V_{\mathrm{ps}}{}^0$ is once more a periodic potential. In fact $V_{\mathrm{ps}}{}^0$ is then identical to the pseudopotential of the pure crystal, so that the kinetic-energy term in the effective-Hamiltonian approach (3.19) is associated with the band structure in the usual way.

Exciton and Impurity States in Rare-Gas Solids*†

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The formalism of the preceding paper is applied to a calculation of the first excited states of (1) pure crystals of Kr and Xe; and (2) rare-gas solids containing a substitutional Xe impurity. A Hartree potential for the bare electron-hole interaction is constructed for each system, and is screened within the random-phase approximation. Matrix elements of the corresponding pseudopotentials, projected according to the Cohen-Heine prescription, are derived in the Wannier representation. Band structures inferred from optical data are fitted to simple interpolation formulas. By transformation to a symmetric representation for the envelope function, the Wannier difference equations are reduced to manageable form and solved by a matrix technique. Although the calculations contain no disposable parameters, obtained binding energies and oscillator strengths are found to be in excellent agreement with experiment.

1. INTRODUCTION

IN the preceding paper[1] the wave-packet theory of exciton and impurity states developed by Wannier and other workers was reviewed. It was asserted that the wave-packet approach, which has been supposed to be valid only for shallow states, in fact could be made to yield satisfactory results for deep states as well, providing that certain microscopic modifications of the customary macroscopic theory were introduced. The purpose of this paper is to examine this statement in detail for the simplest systems containing deep exciton and impurity states, viz., the solid rare gases. For these systems the calculations turn out to be unexpectedly easy, and the results in excellent agreement with experiment. The extension of the methods to other crystals appears to be straightforward.

We begin our presentation in Sec. 2 with an approximate treatment of dielectric screening of the electron-hole interaction in solid rare gases. In Sec. 3 we describe the construction of complete pseudopotentials for the systems studied. Kinetic-energy terms arising from the periodic crystal potential are discussed in Sec. 4, which is followed by a reduction of the Wannier difference equations in Sec. 5. Sections 6 and 7 contain a discussion of the results and comparison with experiment.

2. DIELECTRIC MODEL FOR ISOTROPIC INSULATORS

In Sec. 4 of I we noted that the Fourier components $V_s(q)$ of the self-consistent potential acting between external charges are given by

$$V_s(q) = V_b(q)/\epsilon(q, K=0), \qquad (2.1)$$

where $V_b(q)$ is the Fourier transform of the bare potential. The dielectric function neglecting local field effects is[2]

$$\epsilon(q, K=0) = 1 + \frac{4\pi e^2}{q^2} \sum_{mnk} \frac{|\langle n\,\mathbf{k}+\mathbf{q}\,|\,e^{i\mathbf{q}\cdot\mathbf{r}}\,|\,m\mathbf{k}\rangle|^2}{W_n(\mathbf{k}+\mathbf{q}) - W_m(\mathbf{k})} \qquad (2.2)$$

for insulating crystals, where W_n and W_m are electron and hole band energies, respectively, and

$$\langle n\,\mathbf{k}+\mathbf{q}\,|\,e^{i\mathbf{q}\cdot\mathbf{r}}\,|\,m\mathbf{k}\rangle = \Omega^{-1}\int d\mathbf{r}\,\psi_{n\,\mathbf{k}+\mathbf{q}}{}^*(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}\psi_{m\mathbf{k}}(\mathbf{r}) \qquad (2.3)$$

[1] J. Hermanson and J. C. Phillips, preceding paper, Phys. Rev. 150, 652 (1966), hereafter referred to as I.

[2] N. Wiser, Phys. Rev. 129, 62 (1963).