

Inserting (A4) into (A2) we get

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

which has the symmetry of the lattice.

In the impurity problem (3.18) the core states ϕ_i are not eigenfunctions of crystal momentum and (A6) does not hold. On the other hand, it is easy to see that the

ϕ_i 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_{ps}^0 is once more a periodic potential. In fact V_{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 paper¹ 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

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

where $V_b(q)$ is the Fourier transform of the bare potential. The dielectric function neglecting local field effects is²

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

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

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

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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).

is a transition matrix element connecting the Bloch states $\psi_{m\mathbf{k}}$ and $\psi_{n\mathbf{k}+\mathbf{q}}$; m and n are valence and conduction band indices, respectively, and Ω is the volume of the unit cell. Equation (2.2) corresponds to virtual excitations of electron-hole pairs of momentum q and energy

$$E_{mn}(\mathbf{k}, \mathbf{k}+\mathbf{q}) = W_n(\mathbf{k}+\mathbf{q}) - W_m(\mathbf{k}). \quad (2.4)$$

For solid rare gases only the outer np valence shell need be included in the summation on m in (2.2), since the other shells are more tightly bound, with negligible polarizabilities. Moreover, conduction bandwidths in the rare gases are nearly equal to their free-electron values³; hence, we may replace the $\psi_{n\mathbf{k}}$ by plane waves, as a first approximation (comparison of the calculations of $\epsilon(q,0)$ by Penn⁴ and Nara⁵ for Si shows that exact representation of the $\psi_{n\mathbf{k}}$ is not crucial). Then the matrix element of $e^{i\mathbf{q}\cdot\mathbf{r}}$ is given by the Fourier transform of an np orbital, which decreases sharply for wave vectors not contained in the central Brillouin zone. Thus we may use a two-band model for the polarization, corresponding to retaining only $np \rightarrow (n+1)s$ atomic excitations; oscillator strengths are adjusted to satisfy the sum rule⁶

$$\sum_n |\langle n\mathbf{k}+\mathbf{q} | e^{i\mathbf{q}\cdot\mathbf{r}} | m\mathbf{k} \rangle|^2 E_{mn}(\mathbf{k}, \mathbf{k}+\mathbf{q}) = (\hbar^2/2m)q^2. \quad (2.5)$$

With \mathbf{k} restricted to the first zone, we obtain the approximate result

$$\epsilon(q,0) = 1 + (2\pi\hbar^2 e^2/m) \sum_{\mathbf{k}} [E_{mn}(\mathbf{k}, \mathbf{k}+\mathbf{q})]^{-2}. \quad (2.6)$$

An important characteristic of rare-gas crystals is the large energy gap between valence and conduction bands. This has the effect of reducing the sensitivity of (2.6) both to the shape of the bands and the approximations made to the oscillator strengths. In addition the valence-electron overlap is small, so that the valence bands have small width. For our purposes it is sufficient to represent the pair excitation energies by a free-electron model with a large "zero of the energy." Thus we may write

$$E_{mn}(\mathbf{k}, \mathbf{k}+\mathbf{q}) = E_G + (\hbar^2/2m)(\mathbf{k}+\mathbf{q})^2, \quad (2.7)$$

where E_G is the band gap. Substituting (2.7) into (2.6), we obtain

$$\epsilon(q,0) = 1 + (8\pi m e^2/\hbar^2) \sum_{\mathbf{k}} [(\mathbf{k}+\mathbf{q})^2 + k_0^2]^{-2}, \quad (2.8)$$

where $k_0^2 = 2mE_G/\hbar^2$. In terms of the static dielectric constant ϵ_0 the isotropic part of $\epsilon(q,0)$ is given by

$$\epsilon(q,0) = 1 + (\epsilon_0 - 1)\Sigma(q)/\Sigma(0), \quad (2.9)$$

³ J. C. Phillips, Phys. Rev. **136**, A1714 (1964).

⁴ D. R. Penn, Phys. Rev. **128**, 2093 (1962).

⁵ H. Nara, J. Phys. Soc. Japan **20**, 778 (1965).

⁶ P. Nozières and D. Pines, Phys. Rev. **109**, 741 (1958).

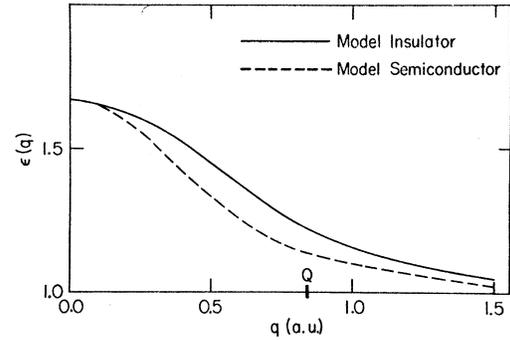


Fig. 1. Dielectric function of argon (atomic units). The solid line is our model for an isotropic insulator, based on a parabolic excitation spectrum. For purposes of comparison, Penn's model for an isotropic semiconductor is shown by the dashed line (based on parameters appropriate to Ar). The "breakdown length" Q^{-1} for the insulator dielectric function is less than the atomic radius of Ar (3.55 a.u.).

where

$$\Sigma(q) = \tan^{-1}\left(\frac{K+q}{k_0}\right) + \tan^{-1}\left(\frac{K-q}{k_0}\right) - \frac{k_0}{2q} \ln \left[\frac{(K+q)^2 + k_0^2}{(K-q)^2 + k_0^2} \right].$$

Here K is the average "radius" of the Brillouin zone, given by

$$\frac{4}{3}\pi K^3 = 8\pi^3/\Omega,$$

and ϵ_0 is set equal to the experimental value.¹³ Equation (2.9) is shown in Fig. 1 as a function of wave number q for Ar; similar results are obtained for the other rare gases.

Our model for an isotropic insulator differs somewhat from Penn's model for an isotropic semiconductor.⁴ The values obtained from his interpolation formula (with the parameters adjusted to Ar) are also shown in Fig. 1. In both models $\epsilon \rightarrow 1$ when $q \rightarrow \infty$, while $\epsilon \rightarrow \epsilon_0$ as $q \rightarrow 0$. Consequently there is no screening of the electron-hole interaction for $r=0$, while $\epsilon(r) \rightarrow \epsilon_0$ for large r , in agreement with macroscopic considerations.⁷ The scale of the breakdown region in real space may be determined from the definition of $\epsilon(r)$:

$$\frac{1}{\epsilon(r)} - \frac{e^2}{r} = P \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{\epsilon(q,0)} w(q) e^{i\mathbf{q}\cdot\mathbf{r}}, \quad (2.10)$$

where $w(q) = 4\pi e^2/q^2$ is the Fourier transform of the Coulomb potential and P denotes the principal part. In order to simplify the integration of (2.10) we replace (2.9) by the simpler function

$$F(q) = 1 + (\epsilon_0 - 1)\alpha^2 K^2 / (q^2 + \alpha^2 K^2);$$

α is chosen to provide a good fit to $\epsilon(q,0)$ and is of order unity for the rare gases. After a trivial contour inte-

⁷ W. Kohn, Phys. Rev. **110**, 857 (1958).

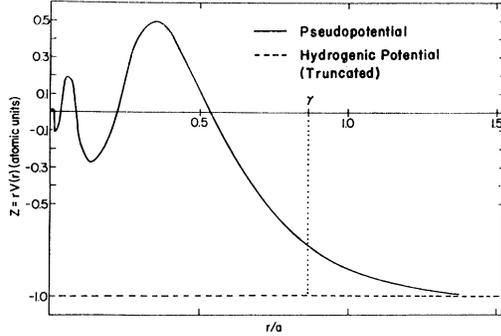


FIG. 2. Unscreened pseudopotential for excitons in Xe. The solid curve was obtained from the Hartree potential by the projection technique of Cohen and Heine. $\gamma = r_0/a$ measures an average radius r_0 of the excluded volume relative to the atomic radius a . The value of r_0 is defined by the requirement that the average of the pseudopotential from 0 to r_0 be zero.

gration we find the result

$$1/\epsilon(r) = 1/\epsilon_0 + [(\epsilon_0 - 1)/\epsilon_0] \exp(-Qr), \quad (2.11)$$

where $Q = \epsilon_0^{1/2} \alpha K$. We note that because E_G is large the breakdown length Q^{-1} is less than the atomic radius. Then $\epsilon(r)$ may be replaced by ϵ_0 outside the central cell. Within the core region of the "impurity" the simple random-phase-approximation (RPA) result is not expected to be valid. On the other hand, the excited electron has almost no amplitude in the region since it must be orthogonal to the core levels (cf. I, Sec. 3). Thus, local field effects can be neglected, and we may write for all r

$$V_s(\mathbf{r} - \mathbf{R}_i) = V_b(\mathbf{r} - \mathbf{R}_i) / \epsilon(|\mathbf{r} - \mathbf{R}_i|), \quad (2.12)$$

where $V_b(\mathbf{r} - \mathbf{R}_i)$ is the unscreened potential.

3. IMPURITY POTENTIALS

Exciton and impurity states satisfy a generalized impurity equation (see I, Sec. 2)

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

where K_0 has full crystal symmetry and V' is an appropriate impurity potential centered about \mathbf{R}_i .

By working in a representation based on the smooth part of ψ (see I, Sec. 3), we found that (3.1) could be rewritten as

$$[K_{ps}^0 + V_{ps}'(\mathbf{r} - \mathbf{R}_i)]\varphi(\mathbf{r} - \mathbf{R}_i) = E\varphi(\mathbf{r} - \mathbf{R}_i), \quad (3.2)$$

where K_{ps}^0 is the pseudopotential kinetic-energy operator for the perfect crystal and V_{ps}' is the "impurity pseudopotential." The smooth function φ is given by

$$\psi = \varphi - \sum_t \phi_t \langle \phi_t | \varphi \rangle \quad (3.3)$$

in terms of the core functions ϕ_t . Because V_{ps}' is small in the cores, interband matrix elements are sharply reduced, so that a one-band approximation for φ is possible. In terms of Wannier functions $\alpha_{n\mathbf{R}}$ derived

from K_{ps}^0 , we may write

$$\varphi(\mathbf{r} - \mathbf{R}_i) = \sum_{\mathbf{R}} F(\mathbf{R}) \alpha_{n\mathbf{R}}(\mathbf{r} - \mathbf{R}_i), \quad (3.4)$$

where n denotes the first conduction band. Inserting (3.4) into (3.2) we have

$$\sum_{\mathbf{R}'} [W(\mathbf{R} - \mathbf{R}') - E\delta_{\mathbf{R}\mathbf{R}'} + V(\mathbf{R}, \mathbf{R}')] F(\mathbf{R}') = 0, \quad (3.5)$$

where

$$W(\mathbf{R} - \mathbf{R}') = \langle n\mathbf{R} | K_{ps}^0 | n\mathbf{R}' \rangle \quad (3.6)$$

and

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

are matrix elements of the crystal and impurity pseudopotentials in the α representation. The model Wannier equations (3.5) are the fundamental equations we wish to solve. The method of solution consists of three steps: (1) We construct a pseudopotential for each system, (2) we compute the matrix elements (3.6), and (3) we solve the secular equation

$$\det \| W(\mathbf{R} - \mathbf{R}') - E\delta_{\mathbf{R}\mathbf{R}'} + V(\mathbf{R}, \mathbf{R}') \| = 0; \quad (3.7)$$

the model amplitude functions $F(\mathbf{R})$ are determined from (3.5). Let us now turn to the calculation of the pseudopotentials.

The impurity potential for a crystal containing a positively charged ion at \mathbf{R}_i is

$$V_0(\mathbf{r} - \mathbf{R}_i) = V_{\text{ion}}(\mathbf{r} - \mathbf{R}_i) - V_{\text{host}}(\mathbf{r} - \mathbf{R}_i), \quad (3.8)$$

where V_{ion} is the screened potential of the ion and V_{host} is the potential of a neutral host atom. The analogous potential for exciton states was derived in I. Because of the tight binding of rare-gas atoms we neglect the motion of the hole; then the exciton potential may also be written in the form (3.8). V_{ps}' is given by the Cohen-Heine prescription⁸:

$$V_{ps}'\varphi = V_0\varphi - \sum_t \phi_t \langle \phi_t | V_0 | \varphi \rangle. \quad (3.9)$$

Because φ is slowly varying in the core region we make the local approximation

$$\begin{aligned} V_{ps}' &= V_0 - \sum_t \phi_t \langle \phi_t | V_0 \rangle \\ &= V_0 + V_R. \end{aligned} \quad (3.10)$$

A convenient prescription for including polarization effects in the impurity potential was given in Sec. 2 in terms of a bare potential $V_b(r)$ and a dielectric constant $\epsilon(r)$. We construct a Hartree potential for V_b :

$$V_b(r) = u_{\text{ion}}(r) - u_{\text{host}}(r), \quad (3.11)$$

where

$$u_{\text{ion}}(r) = -\frac{Z_1 e^2}{r} + e^2 \sum_s' \int d\mathbf{r}' \frac{|\phi_s^{(1)}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad (3.12a)$$

and

$$u_{\text{host}}(r) = -\frac{Z_0 e^2}{r} + e^2 \sum_s \int d\mathbf{r}' \frac{|\phi_s^{(0)}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad (3.12b)$$

are ionic and atomic potentials, neglecting exchange

⁸ M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

and polarization effects. Z_0 and Z_1 denote the atomic number of the host and impurity atoms, while $\phi_s^{(0)}$ and $\phi_s^{(1)}$ are the corresponding core orbitals taken from free-atom calculations.⁹ One np orbital is deleted from the sum in (3.12a) so that $u_{\text{ion}} \sim r^{-1}$ for large r . The self-consistent potential V_0 was derived from Eq. (2.12) for each system, and pseudopotentials V_{ps}' were calculated from (3.10). The unscreened pseudopotential for excitations in Xe is shown in Fig. 2, along with the hydrogenic potential

$$V_H'(r) = -e^2/r. \quad (3.13)$$

As we expected (cf. I) V_{ps}' is greatly reduced in the core region, and approaches the Coulomb law (3.13) outside the cores (the addition of dielectric screening modifies V_{ps}' somewhat). Similar results were found for the other systems.

Before we can solve (3.7) we must compute matrix elements of V_{ps}' in the α representation. According to I we have

$$\alpha_{n\mathbf{R}} = N^{-1/2} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} \varphi_{n\mathbf{k}}, \quad (3.14)$$

where $\varphi_{n\mathbf{k}}$, the smooth part of a Bloch function $\psi_{n\mathbf{k}}$, is an eigenfunction of K_{ps}^0 :

$$K_{ps}^0 \varphi_{n\mathbf{k}}(\mathbf{r}) = W_n(\mathbf{k}) \varphi_{n\mathbf{k}}(\mathbf{r}). \quad (3.15)$$

Because the band structure $W_n(\mathbf{k})$ is approximately given by a free-electron formula³ we may approximate $\varphi_{n\mathbf{k}}$ by a plane wave

$$\varphi_{n\mathbf{k}} = V^{-1/2} \exp(i\mathbf{k}\cdot\mathbf{r}). \quad (3.16)$$

(This will not be true of $\psi_{n\mathbf{k}}$, which must contain an admixture of core functions.) We calculate (3.14) by approximating the first Brillouin zone by a sphere of the same volume (Wigner-Seitz approximation). This leads easily to the result

$$\alpha_{n\mathbf{R}}(\mathbf{r}) = \frac{1}{2\pi^2 \Omega^{1/2}} \left(\frac{\sin K\rho - K\rho \cos K\rho}{\rho^3} \right), \quad (3.17)$$

where $\rho = |\mathbf{r} - \mathbf{R}|$ and K is given by

$$\frac{4}{3}\pi K^3 = (2\pi)^3/\Omega;$$

(3.17) is spherically symmetric about $\mathbf{r} = \mathbf{R}$.

We are now in a position to calculate the potential-energy terms in the difference equations. According to Eq. (3.6) these are given by

$$V(\mathbf{R}, \mathbf{R}') = \int d\mathbf{r} \alpha_{n\mathbf{R}}^*(\mathbf{r}) V_{ps}'(\mathbf{r}) \alpha_{n\mathbf{R}'}(\mathbf{r}). \quad (3.18)$$

Because of the orthogonality of Wannier functions centered about different sites, off-diagonal elements of $V(\mathbf{R}, \mathbf{R}')$ are small for large R , and will be neglected. In addition, the diagonal elements must approach the

⁹ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

TABLE I. Matrix elements of the potential in eV between Wannier functions either in the central cell, $|0\rangle$, or the nearest neighbor, $|d\rangle$. The primary numbers refer to the pseudopotential, whereas the numbers in parentheses refer to the crystal potential ($V_R=0$). For comparison the magnitude of the screened Coulomb potential at the nearest neighbor sites is shown in the last column.

System	$\langle 0 V 0\rangle$	$\langle 0 V d\rangle$	$\langle d V d\rangle$	$-e^2/\epsilon_0 d$
1. Xe in Ne	-1.03 (-4.47)	-0.01 (-0.24)	-3.34 (-4.16)	-4.12
2. Xe in Ar	-1.28 (-3.75)	-0.13 (-0.30)	-1.98 (-2.78)	-2.31
3. Xe in Kr	-1.38 (-3.51)	-0.15 (-0.28)	-1.74 (-2.46)	-1.99
4. Pure Xe	-1.43 (-3.17)	-0.15 (-0.27)	-1.25 (-1.89)	-1.47
5. Pure Kr	-2.18 (-4.24)	-0.225 (-0.35)	-1.84 (-2.57)	-1.99

hydrogenic formula $-e^2/\epsilon_0 R$ for R sufficiently large that V_{ps}' may be assumed constant over a unit cell.

There are three matrix elements for which the continuum approximation

$$\langle \mathbf{R} | V_{ps}' | \mathbf{R}' \rangle = (-e^2/\epsilon_0 R) \delta_{\mathbf{R}\mathbf{R}'}, \quad (3.19)$$

is not suitable. These are:

- (1) The one-center term $\langle 0 | V_{ps}' | 0 \rangle$ (diagonal central-cell correction);
- (2) The two-center nearest-neighbor charge-transfer term $\langle 0 | V_{ps}' | d \rangle$; and
- (3) The dipolar-nearest-neighbor term $\langle d | V_{ps}' | d \rangle$.

Values of these matrix elements are given in Table I for $V = V_{ps}' = V_0 + V_R$. Also shown are values of these quantities computed without orthogonality corrections ($V = V_0$), along with values of $e^2/\epsilon_0 d$. We note that all matrix elements are substantially reduced by the inclusion of V_R in the impurity potential, and that the reduction is greatest when the size disparity between impurity and host atoms is greatest (Xe in Ne). These "excluded volume effects" will be shown below to play a dominant role in interpreting the observed trends in binding energies and oscillator strengths.

4. INTERBAND KINETIC ENERGY

The kinetic-energy terms $W(\mathbf{R} - \mathbf{R}')$ of Eq. (3.5) are, in terms of the band structure of the host lattice,

$$W(\mathbf{R} - \mathbf{R}') = N^{-1} \sum_{\mathbf{k}} [W_n(\mathbf{k}) - W_m(\mathbf{k})] e^{i\mathbf{k}\cdot(\mathbf{R} - \mathbf{R}')}, \quad (4.1)$$

where $W_n(\mathbf{k})$ and $W_m(\mathbf{k})$ are band structures for the electron and hole, respectively, [we set $W_m(\mathbf{k})$ equal to a constant for impurity states or trapped excitons] and the \mathbf{k} -space sum is restricted to the first Brillouin zone. In Fig. 3 we show the band structure of solid Xe as inferred⁸ from Baldini's optical data. The important features are the flat valence bands, the wide conduction band, and the large spin-orbit splitting in

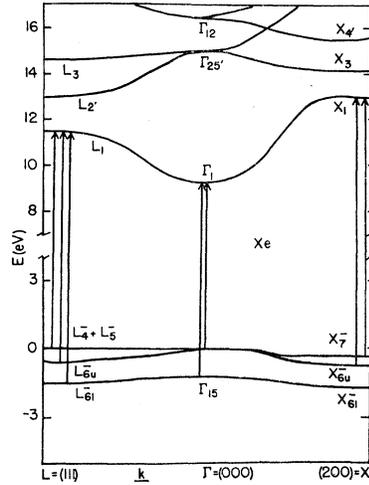


FIG. 3. Band structure of Xe, as inferred from optical data. The double-group notation is used for the valence bands, the single-group for the conduction bands.

the valence bands. In order to simplify the calculation of $W(\mathbf{R}-\mathbf{R}')$ we employ an interpolation model for the band structure:

$$W_n(\mathbf{k}) - W_m(\mathbf{k}) = E_G + \frac{1}{3}E_L [3 - \cos(\frac{1}{2}ak_x) \cos(\frac{1}{2}ak_y) - \cos(\frac{1}{2}ak_x) \cos(\frac{1}{2}ak_z) - \cos(\frac{1}{2}ak_y) \cos(\frac{1}{2}ak_z)], \quad (4.2)$$

where a is the lattice parameter, E_G the energy gap, and E_L the bandwidth at L .

According to Phillips' nearly free electron model for the conduction bands,¹⁰

$$E_L = E_f(L) - S_L/2 = 3\hbar^2/8ma^2 - S_L/2, \quad (4.3)$$

where $E_f(k) = \hbar^2 k^2/2m$ and S_L is the nearly free electron splitting of the L_1 and $L_{2'}$ levels. In Xe $E_f(L)$ is 2.9 eV, and S_L determined spectroscopically is 1.4 eV, so that E_L is 2.2 eV. Spectroscopic data to determine S_L are not available for Ne, Ar, or Kr.

To determine S_L in these crystals we make use of the chemical trends in s - p splittings which are manifested in several ways. In the alkali metals¹¹ the s - p splitting at $\mathbf{k}=\mathbf{N}$ decreases from Li to Cs, reversing sign between Na and K. Also low-energy electron scattering from rare-gas atoms is characterized¹² by

TABLE II. Microscopic parameters used to determine chemical shifts in conduction-band models for the family of rare-gas solids.

Element	f_0 (a.u.)	S_L (eV)	E_L (eV)	$(\mu^*/m)^a$	$(\mu/m)^b$
He	1.19
Ne	0.24	0	5.6	...	0.40
Ar	-1.70	0.4	3.8	0.46	0.43
Kr	-3.7	0.8	3.1	0.41	0.46
Xe	-6.5	1.4	2.2	0.31	0.54

^a Deduced by Baldini from Rydberg series for $n \geq 2$.

^b From curvature of our model $W(k)$ near $k=0$.

¹⁰ J. C. Phillips, Phys. Rev. **136**, A1705 (1964).

¹¹ N. Ashcroft, Phys. Rev. **140**, A935 (1965).

¹² T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).

the lengths f_0 shown in Table II. Again a sign reversal occurs, and in the atoms adjacent to those for which the alkali s - p splitting reverses sign. Thus we assume that S_L vanishes for Ne and interpolate linearly between Ne and Xe to obtain the Ar and Kr values also shown in Table II. Note that although (4.2) has the form of a tight-binding expansion, the parameter E_L is determined primarily by $E_f(L)$, as can be seen in Table II, and not by interatomic overlap integrals.

The tight-binding form assumed for (4.2) reduces near $\mathbf{k}=0$ to $\text{const} + \frac{1}{2}E_L(ka)^2$ or $\text{const} + \frac{1}{2}(\hbar k)^2\mu$ with μ/m listed in Table II. These values of μ/m disagree significantly with the continuum values of μ^*/m deduced by Baldini from a hydrogenic model of the $n=2, 3$ levels.¹³ It is evident that our single parameter E_L cannot reproduce both the bandwidth and $(\mu^*)^{-1}$, the curvature near $k=0$, correctly. A correction is made for this deficiency in the calculations discussed later.

5. REDUCTION OF WANNIER EQUATIONS

It is convenient to transform to a representation based on symmetrized linear combinations of the $\alpha_{\mathbf{R}\mathbf{R}}$. Any two of the transformed basis functions have vanishing matrix elements coupling them unless both functions have the same symmetry under an appropriate subgroup of the point group of the crystal; thus the secular equation may be factorized into sets of equations having lower dimensionalities. The correct symmetry group may be determined from inspection of the Wannier equations (3.5). Each interband edge may generate bound states; if the interband edge is degenerate (as in many-valley semiconductors), supermultiplets will be formed which will exhibit a so-called valley-orbit splitting consistent with that subgroup of the full point group which interchanges the band edges.

Fortunately, in rare-gas solids by neglecting the valence bandwidth we can deal with a nondegenerate interband edge at $\mathbf{k}=\mathbf{\Gamma}=0$ for both excitons and impurities. We are interested only in s exciton states because the transition $\Gamma_{15} \rightarrow \Gamma_1$ is dipole allowed. Similarly for the impurity states we calculate only s states and assume that ns and np states of the impurity are degenerate, so that $1s \rightarrow np$ excitation energies can be obtained from a knowledge of the positions of the s levels alone.

The s states are the totally symmetric linear combinations γ_s of the Wannier functions $\alpha_{\mathbf{R}\mathbf{S}}$:

$$\gamma_s(\mathbf{r}) = N_s^{-1/2} \sum_{\mathbf{R}\mathbf{S}} \alpha_{\mathbf{R}\mathbf{S}}(\mathbf{r}), \quad (5.1)$$

where the sum is over lattice vector belonging to the S th "star" containing N_s members, and we have

$$\varphi(\mathbf{r}-\mathbf{R}_i) = \sum_{\mathbf{S}} G_{\mathbf{S}} \gamma_{\mathbf{S}}(\mathbf{r}-\mathbf{R}_i), \quad (5.2)$$

where $G_{\mathbf{S}} = N_s^{1/2} F(|\mathbf{R}_{\mathbf{S}}|)$. It is easy to show that the

¹³ G. Baldini, Phys. Rev. **128**, 1562 (1962).

transformation (5.1) is unitary. Equations (3.5) are replaced by

$$\sum_{S'} H_{SS'} G_{S'} = E G_S, \quad (5.3)$$

where $H_{SS'} = W_{SS'} + V_{SS'}$ with the definitions

$$W_{SS'} = (N_S N_{S'})^{-1/2} \sum_{\mathbf{R}_S \mathbf{R}_{S'}} W(\mathbf{R}_S - \mathbf{R}_{S'}), \quad (5.4a)$$

$$V_{SS'} = (N_S N_{S'})^{-1/2} \sum_{\mathbf{R}_S \mathbf{R}_{S'}} V(\mathbf{R}_S, \mathbf{R}_{S'}). \quad (5.4b)$$

In this “ γ representation” we have one basis function for each distinct star of lattice vectors, and the dimensionality of the secular equation is reduced by a factor of about 20. An expansion of φ out to 30 or 40 shells is now possible, so that this formalism is appropriate to the study of “intermediate” excitons (e.g., in alkali halides and rare-gas solids). Recalling the identity

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

it is easy to show that

$$W_{SS'} = \sum_{S''} A_{S''} \sum_{\mathbf{R}_S \mathbf{R}_{S'} \mathbf{R}_{S''}} \delta_{\mathbf{R}_{S''}, \mathbf{R}_S - \mathbf{R}_{S'}}, \quad (5.5)$$

where A_S is defined in the expansion

$$W_n(\mathbf{k}) - W_m(\mathbf{k}) = \sum_S A_S (N_S)^{-1/2} \sum_{\mathbf{R}_S} e^{i\mathbf{k} \cdot \mathbf{R}_S}. \quad (5.6)$$

The expansion (5.6) is always possible because of the continuity and cubic symmetry of $(W_n - W_m)$. In our tight-binding model there are only two nonvanishing coefficients A_S representing the energy gap and the bandwidth. Equation (5.5) for the kinetic-energy terms is convenient because it contains no \mathbf{k} -space integration [see Eq. (4.1)]. As before, the energy gap appears only along the diagonal ($S=S'$) and may be set equal to zero; then $W_{SS'}$ is linear in E_L [the lattice sums in (5.5) depend only upon crystal symmetry]. Since E_L decreases with increasing atomic number, the density of states at the interband edge increases with Z , which in turn has the effect of enhancing binding energies for large Z . This trend, however, is reversed by the Z -dependence of ϵ_0 , which increases^{13,14} from 1.1 for Ne to 2.23 for Xe.

6. EXCITONS IN Xe AND Kr

We are now in a position to solve the Wannier difference equations (3.5) using both a realistic band structure and an interaction which include three corrections to the hydrogenic problem: (1) Breakdown of macroscopic dielectric screening in the central cell or spatial dispersion (DB), (2) nonparabolic energy bands (KE), and (3) repulsive terms in the central cell (R). Corrections (1) and (2) were previously considered by Kohn and Luttinger¹⁵; when $m^*/m \ll 1$ both corrections produce negative shifts of the 1s energies below their

hydrogenic values. Correction (3) arises from the orthogonality terms discussed in the preceding paper.

Before solving the difference equations carefully we wish to illustrate the relative magnitude of these three terms by solving a model differential equation, treating these effects by first-order perturbation theory. We know that for the exciton states the hydrogenic model works very well. Our unperturbed wave function is therefore the hydrogenic 1s state described by Baldini¹³:

$$\psi_{1s}(r) = (\pi/a_0)^{3/2} e^{-r/a_0}, \quad (6.1)$$

where $a_0 = (\hbar^2/mc^2)[\epsilon_0/(\mu^*/m)]$ is the first Bohr radius according to the effective-mass approximation¹⁶ (EMA). We construct a model Hamiltonian which contains, in a qualitative way, the effects due to DB, KE, and R:

$$H_M = K_M + V_{M'}. \quad (6.2)$$

The kinetic-energy operator

$$K_M = -\frac{\hbar^2}{2m} \times \frac{1}{2} \left(\frac{m}{\mu(r)} \nabla^2 + \nabla^2 \frac{m}{\mu(r)} \right) \quad (6.3)$$

contains the effects of large- k variation of μ^* ; $\mu(r)$ is a radially-dependent effective mass described below. Corrections due to spatial dispersion and repulsive terms in the central cell are contained in a model potential

$$V_{M'} = [-e^2/\epsilon(r)r][1 - \theta(r - r_0)]. \quad (6.4)$$

Except for the radial dependence of the dielectric constant, $V_{M'}$ is a hydrogenic potential for $r > r_0$; we assume that cancellation between V' and $V_{R'}$ is exact for $r < r_0$, the radius of the “excluded volume.”

Interpolation formulas were constructed for the radial dependences of $\mu(r)$ and $\epsilon(r)$. The formulas give correct limiting behavior for $r \rightarrow \infty$ and $r \rightarrow 0$, with exponential interpolation between the limits, characterized by decay factors which scale with the lattice constant. Variation of the dielectric constant was chosen to be of the form

$$1/\epsilon(r) = 1/\epsilon_0 + [(\epsilon_0 - 1)/\epsilon_0] \exp(-Qr), \quad (6.5)$$

where $Q = K_F$ is the Fermi wave number. Note that $\epsilon(r)$ approaches 1 for small r and ϵ_0 for large r , and that Q^{-1} plays the role of a characteristic “breakdown” length for an insulator. Qualitatively the variation of effective mass (in real space) can be described in terms of μ^* , the macroscopic ($k \rightarrow 0$) effective mass, by

$$m/\mu(r) = m/\mu^* - (m/\mu^* - 1) \exp(-r/a). \quad (6.6)$$

For small r , $\mu(r)$ tends to the free-electron value m , whereas $\mu(r) \rightarrow \mu^*$ as $r \rightarrow \infty$. Note that $r = a$ is associated with wave number $k = 2\pi/a$, so that a^{-1} is a characteristic decay factor for the effective mass. The pertinent microscopic quantities Q and a^{-1} are given

¹³ G. Baldini, Phys. Rev. **137**, A508 (1965).

¹⁵ W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

¹⁶ W. Kohn, Solid State Phys. **5**, 257 (1957).

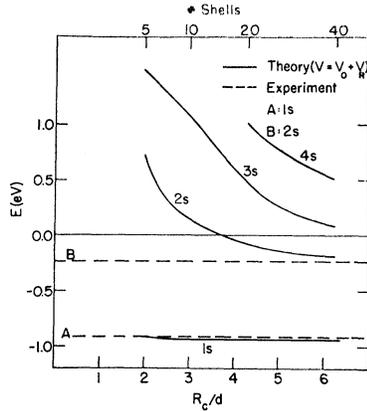


FIG. 4. Convergence of exciton energies for Xe. R_c is the cutoff radius defined in the text. The observed energies of the 1s and 2s states are given by the dashed lines A and B. For $R_c \rightarrow \infty$ a Rydberg series for $n \geq 2$ is expected.

in Table III. Also shown is a third parameter $\gamma = r_0/A$, the equivalent radius of the excluded volume according to first-order perturbation theory, relative to the atomic radius A [see Eq. (6.4)].

With the above interpolation formulas the model Hamiltonian (6.2) can be written as

$$H_M = H_{EMA} + H_{CC}, \quad (6.7)$$

where $H_{EMA} = -(\hbar^2/2\mu^*)\nabla^2 - e^2/\epsilon_0 r$ is the macroscopic Hamiltonian,¹⁶ and

$$H_{CC} = V_{DB} + V_{KE} + V_R$$

contains the central cell corrections. Here

$$V_{DB} = -[(\epsilon_0 - 1)/\epsilon_0](e^2/r)[1 - \theta(r - r_0)] \times \exp(-Qr) \quad (6.8a)$$

represents spatial dispersion for $r > r_0$ and vanishes for $r < r_0$; corrections for the nonparabolic nature of the energy bands are contained in the term

$$V_{KE} = -\frac{\hbar^2}{2m} \left(\frac{m}{\mu^*} - 1 \right) \times \left(\frac{\exp(-r/a)\nabla^2 + \nabla^2 \exp(-r/a)}{2} \right) \quad (6.8b)$$

and

$$V_R = (e^2/\epsilon_0 r)\theta(r - r_0) \quad (6.8c)$$

is the effective (local) repulsive potential.

We are now in position to calculate the first-order corrections to the hydrogenic theory. According to the Kohn-Luttinger model the energy shift is¹⁵

$$\Delta E_{KL} = \langle V_{DB} \rangle + \langle V_{KE} \rangle, \quad (6.9)$$

TABLE III. Microscopic parameters for Kr and Xe (atomic units) in simplified quasi-hydrogenic model.

Crystal	Q (DB)	a^{-1} (KE)	$\gamma = r_0/A$ (R)
Kr	0.6	0.094	0.80
Xe	0.5	0.086	0.86

TABLE IV. Energy shifts of 1s excitons in Kr and Xe [in units of $|E_H(1s)| = \mu^* e^4 / 2\epsilon_0^2 \hbar^2$] as computed from simplified model. The terms $\langle V_{DB} \rangle$, $\langle V_{KE} \rangle$, and $\langle V_R \rangle$ are defined in the text. The sum of the first two gives an estimate ΔE_{KL} of the hydrogenic defect according to the Kohn-Luttinger methods (Ref. 16). The sum of all three terms gives ΔE . The relative hydrogenic defects observed experimentally are given in column 6.

Crystal	$\langle V_{DB} \rangle$	$\langle V_{KE} \rangle$	$\langle V_R \rangle$	ΔE_{KL}	ΔE	ΔE_{exp}
Kr	-0.06	-0.55	+0.92	-0.61	+0.31	+0.13
Xe	-0.07	-0.51	+0.53	-0.58	-0.05	-0.07

whereas according to the theory of the preceding paper,

$$\Delta E = \langle V_{DB} \rangle + \langle V_{KE} \rangle + \langle V_R \rangle. \quad (6.10)$$

The calculated shifts $\langle V_{DB} \rangle$, $\langle V_{KE} \rangle$, and $\langle V_R \rangle$ are given in Table IV, along with ΔE_{KL} and the total shift ΔE , for 1s excitons in Kr and Xe. The experimental shifts are presented in the same table. We see that the positive contribution $\langle V_R \rangle$ is large, and that in spite of considerable cancellation the predicted shifts agree in sign with the rather small hydrogenic defects for both crystals. Thus, the unexpected success of the EMA for excitons in Kr and Xe is due to the substantial cancellation between central cell corrections.

We expect generally that the hydrogenic theory will be useful for deep exciton states in other filled-shell insulators such as alkali halides. For deep impurity states (e.g. Xe in Ar) the above cancellation may not be so complete because the potential of the impurity ion differs significantly from that of an ionized atom of the host crystal. Thus, because the Xe ion is larger than an Ar atom the excluded volume correction $\langle V_R \rangle$ outweighs the negative corrections $\langle V_{KE} \rangle$ and $\langle V_{DB} \rangle$, which are only slightly changed by the replacement of an Ar ion by a Xe ion, and the hydrogenic defect is large and positive.^{14,17} In semiconductors, on the other hand, the valence shell is only half-filled and the excluded volume associated with the core is small. Thus (cf. I) the 1s donor binding energies are larger than the EMA result.

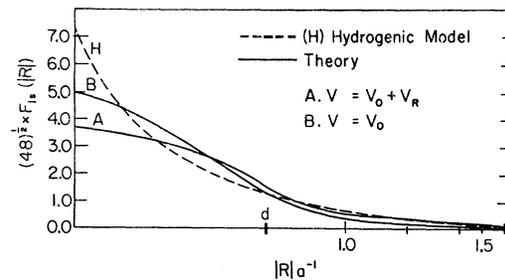


FIG. 5. Envelope function for 1s exciton in Kr. The hydrogenic envelope function is given by the dashed line. The solid curves are solutions of the difference equations for $n=1$. Curve A includes the effects of the repulsive potential while curve B does not. The nearest-neighbor distance is d .

¹⁷ G. Baldini and R. S. Knox, Phys. Rev. Letters **11**, 127 (1963).

TABLE V. Hydrogenic defects of $1s$ excitons in Kr and Xe obtained from the Wannier equations relative to $|E_H(1s)|$. The first column contains results for $V_R=0$. Results obtained with the pseudopotential $V_{ps}'=V_0+V_R$ are given in column 2, and the experimental results are listed in column 3.

Crystal	$\Delta E (V=V_0)$	$\Delta E (V=V_0+V_R)$	ΔE (exp)
Kr	-0.80	+0.15	+0.13
Xe	-1.76	-0.09	-0.07

The model calculation has shown the relative magnitude of DB, KE, and R corrections to the macroscopic theory, and has led to a qualitative understanding of the success of the EMA. However, the use of a differential equation to represent the Wannier equations is not valid¹⁸ for $(a_0/a)^2 \lesssim 1$; in the calculation of deep states the finite spread of the Wannier function must be taken into account. We saw in Sec. 3, for example, that certain two-center corrections are not negligible, and that calculated matrix elements differ significantly from $-e^2/\epsilon_0 R$ for $R \lesssim d$, the nearest-neighbor distance. Consequently we must solve the Wannier equations (5.3); we do this by truncating and solving the secular equation. In the remainder of this section we present the results of calculations of $1s$ excitons in Kr and Xe; calculations of deep impurity states of Xe in Ne, Ar, and Kr will be summarized in Sec. 7.

Before solving the difference equations we recall that exciton states with $n \geq 2$ will not be given correctly by the solutions, because the curvature of our model energy bands is given incorrectly near $k=0$ (cf. Sec. 4). Since the $1s$ state will be orthogonal to these higher states, it is desirable to modify the equations in such a way that they are given correctly. We do this by renormalizing the macroscopic potential terms (3.19): we replace ϵ_0 by $\epsilon_0' = (\mu|\mu^*)^{1/2}\epsilon_0$ ($\approx 1.3\epsilon_0$ for Kr and Xe); for $R \lesssim d$ large- k behavior of the energy bands is important, and we retain the matrix elements of V_{ps}' listed in Table I. The calculations show that the effective Bohr radius for $1s$ states is less than d , so that the

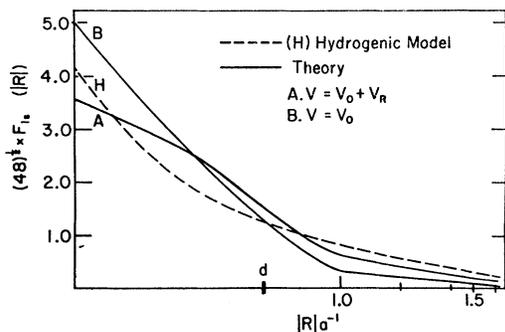


FIG. 6. Envelope function for $1s$ exciton in Xe. The notation is the same as Fig. 5.

¹⁸ E. N. Adams, Phys. Rev. 85, 41 (1952).

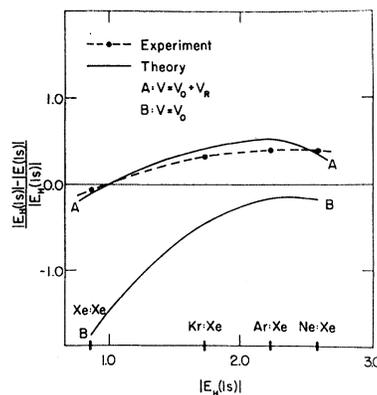


FIG. 7. Relative hydrogenic defects of the $1s$ state of a Xe impurity in various host lattices. The abscissa is $|E_H(1s)|$, the hydrogenic binding energy, which is a measure of the strength of the electron-hole coupling neglecting central cell corrections. Experimental defects are joined by the dashed line; theoretical curve A passes close to the experimental shifts. Curve B indicates the results obtained without the repulsive potential V_R . The agreement between theory and experiment is qualitatively poor for curve B, which predicts that the hydrogenic defect is always negative.

replacement $\epsilon_0 \rightarrow \epsilon_0'$ results only in slight modifications of the "tail" of the wave function.

Calculated hydrogenic defects for $1s$ excitons in Kr and Xe are listed in Table V. For comparison we list the defects obtained by neglecting the repulsive term V_R in the same table. The agreement between calculated and observed defects is excellent for the pseudopotential theory ($V=V_0+V_R$); the agreement is poor for $V=V_0$. Again, the occurrence of small defects is seen to be a consequence of the orthogonality requirement; the Schmidt terms in the impurity function $\psi(\mathbf{r}-\mathbf{R}_i)$ correspond to a large, positive kinetic energy which cancels the negative corrections (DB and KE).

The convergence of these results with respect to the number of basis functions is indicated in Fig. 4 for Xe. R_c is the cutoff radius for the expansion of the model wave function φ in terms of Wannier functions. We note that the $1s$ energy has converged at $R_c \approx 3d$, while the larger $2s$ state must be expanded out to $R_c \approx 6d$ (40 shells) before convergence is indicated; the $2s$ energy appears to converge toward the experimental value of -0.23 eV.

Calculated $1s$ envelope functions are shown in Figs. 5 and 6, along with the EMA function (6.1). Once again the repulsive term V_R plays a fundamental role in the

TABLE VI. Oscillator strength ratio $r = f_{1s}/f_{2s}$ for excitons in Kr and Xe. The first column contains the hydrogenic value, and columns 2 and 3 contain results obtained from the Wannier difference equation for $V=V_0$ and $V=V_0+V_R$, respectively. The last column lists values of r deduced by Baldini.

Crystal	r (EMA)	$r (V=V_0)$	$r (V=V_0+V_R)$	r (exp)
Kr	8	10.7	8.0	4.0
Xe	8	11.0	9.0	9.0

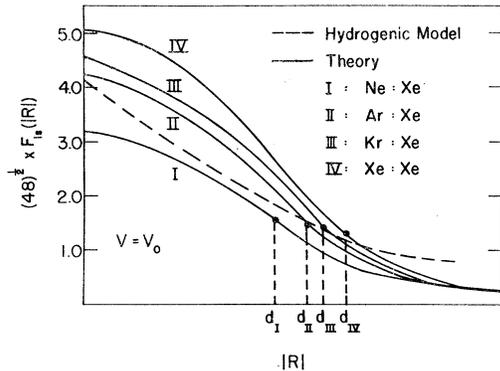


FIG. 8. Envelope function for the $1s$ state of a Xe impurity in various rare-gas host lattices. Orthogonality corrections to the impurity potential were neglected ($V=V_0$) in these calculations. The dashed line is the hydrogenic envelope function for the $1s$ exciton in Xe and d_J is the nearest-neighbor distance in the J th system.

result; comparison of wave functions A ($V=V_0+V_R$) and B ($V=V_0$) illustrates the reduction of amplitude in the central cell brought about by the repulsive term V_R . In addition to diminishing the binding energy, this effect lowers the oscillator strength¹⁹:

$$f_{ns} \sim |F_{ns}(0)|^2. \quad (6.11)$$

In Table VI we list the ratio $r=f_{1s}/f_{2s}$ calculated from (5.3) and (6.11) ($R_c=6d$) and compare with the hydrogenic prediction and experiment.¹³ Because V_R reduces $F_{2s}(0)$ as well as $F_{1s}(0)$ the calculated ratio of oscillator strengths is nearly given by the EMA result. Agreement of the calculated ratio and experiment is excellent for Xe but not for Kr; in the latter case the experimental ratio is less certain because of greater lifetime broadening.

7. DEEP IMPURITY STATES

The availability of optical data^{14,17} on the first excited states of a substitutional Xe impurity in crystals of Ne, Ar, and Kr makes it possible to study the dependence of exciton binding on the macroscopic parameters ϵ_0 and μ^* . For $n \geq 2$ this dependence is given by the hydrogenic formula because the effective Bohr radii for these states are large compared with the atomic radius. For $n=1$, on the other hand, there is only a weak dependence of binding energy on ϵ_0 and μ^* , indicating that the wave function is confined to the neighborhood of the Xe impurity. Thus it is important that these deep states be calculated from the microscopic theory developed above; in this section we present the results of this calculation.

Hydrogenic defects of the first excited state ($1s$) of Xe were calculated for the systems (I) Xe in Ne, (II) Xe in Ar, (III) Xe in Kr, and (IV) pure Xe (cf. Sec. 6). The results shown in Fig. 7 are plotted against the

¹⁹ R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

EMA binding energy $|E_H(1s)|$ and are normalized by the same factor. Comparison of curves A ($V=V_0+V_R$) and B ($V=V_0$) shows once again the crucial role played by the repulsive terms in the central cell. The agreement between the pseudopotential theory (curve A) and experiment is excellent over the entire range of interaction strength, from pure Xe, where $|E_H(1s)|=0.86$ eV, to Xe in Ne, where $|E_H(1s)|=2.59$ eV.

As expected (cf. Sec. 6), the repulsive term outweighs the negative corrections to the EMA in I, II, and III, and large positive defects are observed; in IV the cancellation between central cell corrections is nearly exact.

The influence of the repulsive terms can be more clearly seen in the envelope functions. Solutions of the difference equations for the $1s$ states are given in Figs. 8 and 9. In both figures, the amplitude at the nearest neighbor site indicated by d_J increases relative to the amplitude at the origin as ϵ_0 decreases (i.e., as the interaction strength outside the central cell increases). In Fig. 8 ($V=V_0$), all systems except I show enhanced amplitude at $R=0$ relative to the hydrogenic value, because of DB and KE (negative) corrections to the binding energy. Figure 9 includes the effects of the repulsive term V_R in addition to the above corrections; $F_{1s}(0)$ is depressed compared to the hydrogenic value in all cases. Because of the latter reduction we expect the oscillator strength ratio $r=f_{1s}/f_{2s}$ to be less than the hydrogenic value (8:1) and that this ratio will increase with the atomic number of the host [i.e., as $F_{1s}(0)$ increases]. Values of r computed from Eq. (6.12) using solutions of the Wannier equations for $R_c=6d$ are given in Fig. 10, together with values of this quantity estimated from the optical data by comparing the area under the absorption peaks for $n=1$ and $n=2$. Agreement between our pseudopotential theory and experiment is excellent for all cases. As expected, the reduction of r from the hydrogenic result is greatest for case I (Xe in Ne) where the ratio of

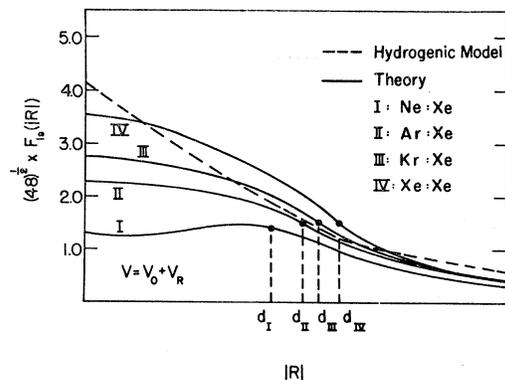


FIG. 9. Envelope function for the $1s$ state of Xe in various host lattices, calculated with the pseudopotential $V=V_{ps}'=V_0+V_R$. Note that the central cell amplitude is reduced from Fig. 8, due to the repulsive term V_R .

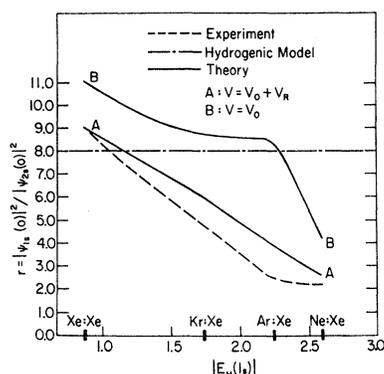


FIG. 10. Oscillator strength ratio for a Xe impurity in several rare-gas environments. $r = (f_{1s}/f_{2s})$ is given by the ratio of central cell amplitudes for $n=1$ and $n=2$. According to the hydrogenic theory r has the constant value 8.0 independent of environment. Curve A was obtained by solving the Wannier equations with $V = V_{ps}' = V_0 + V_R$, and the experimental results are given by the dashed line. The disagreement between theory and experiment for Xe in Ar and Xe in Kr is thought to be due primarily to uncertainties in the band structures assumed for these crystals.

impurity "volume" to the atomic volume of the host is largest.

8. DISCUSSION

We have applied the pseudopotential theory of exciton and impurity states developed in I to a calculation of (1) $1s$ excitons in Kr and Xe, and (2) $1s$ states of a Xe impurity in Ne, Ar, and Kr. Three corrections to the hydrogenic theory were considered: (a) spatial dispersion, (b) large- k variation of the effective mass, and (c) repulsive terms in the central cell, representing core parts of the impurity function. To determine the relative magnitude of each effect a model Hamiltonian based on simple interpolation formulas was constructed. First-order corrections to the hydrogenic theory were calculated; the total energy shifts agreed in sign with the experimental shifts. Because each contribution (a)–(c) could be evaluated separately it was possible to obtain a qualitative understanding of the remarkable success of the effective mass approximation for excitons in Kr and Xe. Specifically, it was shown that the positive correction due to the effective repulsive potential cancels the negative contributions (a) and (b) to a large extent, with the result that the hydrogenic defect is small.

In order to verify the results of the model calculation the Wannier difference equations were solved by a matrix technique. The calculated binding energies and oscillator strengths were in excellent agreement with experiment in all cases. To our knowledge this is the

first time that the Wannier wave-packet approach has been shown to yield good results for deep states in insulating crystals. From our results one may conclude that the neglect of exchange- and local-field corrections to the electron-hole interaction is justified, and non-local terms in the exciton Hamiltonian may be neglected. Finally, the representation of the energy bands by our simple interpolation formula does not produce serious errors. (With additional computational effort and at the expense of simplicity it would be possible to improve further the treatment of the kinetic-energy terms.) Thus, if we were to choose a smaller bandwidth for Ar or Kr [as Mattheiss's augmented plane wave (APW) calculations²⁰ have suggested] the enhanced density of states at the interband threshold would lead to stronger binding and, consequently, better agreement with experiment. We note that our calculations for Xe and Ne, for which the band structure is more certain (cf. Sec. 4), are in essentially exact agreement with experiment—even the anomalous oscillator-strength ratio for Ne:Xe (2:1 rather than 8:1) is given correctly.

The success of our calculations for parabolic excitons indicates that the electron-hole potential we constructed is good over the entire range of r . Thus we are in a position to calculate excitons derived from higher conduction bands^{21,22} as well as scattering resonances associated with critical points in the interband density of states that lie above the fundamental edge. Phillips²³ has suggested that peak structure observed in the insulators above threshold may often be interpreted in terms of such resonances. Calculations based on this suggestion are being carried out by the author.

Extension of the methods of this paper to the alkali halides is straightforward. The conduction bands of the two systems are similar, so that the treatment of kinetic-energy terms needs only slight modification (viz., inclusion of a width for the halide valence bands). From the results of this paper one would anticipate that exciton states in the alkali halides should follow a hydrogenic pattern, especially in those crystals, such as KBr, RbBr, KI, and RbI, whose bands closely resemble those of the solid rare gases.¹⁰

ACKNOWLEDGMENT

It is a pleasure to thank Professor J. C. Phillips for suggesting the problem, and invaluable advice and encouragement during all phases of its execution.

²⁰ L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

²¹ A. W. Overhauser, Phys. Rev. **101**, 1702 (1956).

²² R. S. Knox and N. Inchauspe, Phys. Rev. **116**, 1093 (1959).

²³ J. C. Phillips, Phys. Rev. Letters **12**, 142 (1964).