

LCAO Treatment of Exciton Structure in Alkali Halide Crystals*

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A Heitler-London treatment is applied to the transfer mechanism which has been traditionally associated with the fundamental absorption of alkali halide crystals. In particular, detailed calculations are made for NaCl using the free atom Na 3s Hartree-Fock solution for the one-electron transfer function and the free ion Hartree-Fock solutions for the remaining one-electron functions. The energy and oscillator strength so determined are irreconcilable with experiment showing that the free atom Na 3s function cannot be used in conjunction with the transfer model if the model is to yield sensible results. In a very semiquantitative way it is shown that an electron-hole overlap integral of about 0.1 coupled with Overhauser's exciton model leads to a doublet structure which is in agreement with experimental results for many of the chlorides, bromides, and iodides. These findings do not distinguish the transfer model from the "excitation model."

I. INTRODUCTION

THEORETICAL studies of the fundamental absorption of alkali halide crystals have been based on two different models. The "electron transfer model" presupposes the primary absorption process to be the transfer of an outer shell electron from a lattice anion to a nearest neighbor cation, leaving the halogen atom in the ground-state configuration. Using this model, Klemm¹ and von Hippel,² within the limits of a classical approach, were able to obtain satisfactory agreement with the observed position of the absorption peak in most of the alkali halide crystals. The transfer model has been extended by Overhauser³ in a group theoretic treatment of the multiplet structure of exciton absorption lines. Dexter,⁴ in his calculations of the absorption cross section associated with exciton creation in NaCl, assumed localization of the excited electron in a 4s state on the same chlorine site as the hole, and has referred to this as the "excitation model."⁵ Muto and Okuno⁶ have studied this model in great detail for KCl and more recently it has been studied for the remaining alkali chlorides.⁷ Both models are subject to criticism. For example, in the work of Klemm and von Hippel questionable assumptions are made concerning the polarizability of the alkali and halogen ions and atoms. The work of Muto and Okuno is essentially an application of the Wannier theorem in which the dielectric constant and effective mass near the bottom of the conduction band play the role of parameters. Judicious choice of these parameters yields results in accord with experiment. However, the choice of parameters implies an electron-hole separation of about 2.5 Bohr radii which is by no means large relative to a lattice con-

stant, so that validity of the Wannier theorem is questionable in this instance.

On the basis of the excitation model, Muto et al.⁷ have predicted a multiplicity exceeding the doublet structure. In their analysis, the Wannier functions describing the hole belong to the irreducible representation Γ_4' (here the notation of reference 3 is used), while the excited one electron function is a basis for Γ_1 . The singlet spin function of the electron and hole belongs to Γ_1 , while the triplet spin functions belong to Γ_4 . The product representations are, therefore,

$$\Gamma_4' \times \Gamma_1 \times \Gamma_1 = \Gamma_4',$$

$$\Gamma_4' \times \Gamma_1 \times \Gamma_4 = \Gamma_1' + \Gamma_3' + \Gamma_4' + \Gamma_5'.$$

Since the perturbation operator for an optical dipole transition belongs to Γ_4' , we see that the excitation model (as applied by Muto, Oyama, and Okuno) will not yield a multiplicity exceeding the doublet structure.

No treatment to date based on either model has taken into account exchange energy associated with the overlapping of the excited electron with its neighboring electrons. In Sec. II, the electron transfer model is treated in the spirit of a Heitler-London approximation. The calculations are applied to NaCl using the free atom Na 3s Hartree-Fock⁸ solution for the one electron transfer function and the free ion Hartree-Fock⁹ solutions for the remaining one-electron functions. Correlation effects, other than exchange, are taken into account by a classical treatment in which the dielectric constant (κ) of the material appears as a parameter. In the absence of overlap and exchange effects, and choosing κ equal to its high-frequency value for NaCl, a value of 7.8 eV is obtained for the excitation energy. Agreement with the room-temperature value of 7.7 eV is fortuitous, however, since inclusion of overlap and exchange effects of the excited electron with its nearest neighbor Cl- 3p and 3s electrons yields an excitation energy about 8 eV too high. These results indicate that

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² A. von Hippel, Z. Physik **101**, 680 (1936).

³ A. W. Overhauser, Phys. Rev. **101**, 1702 (1956).

⁴ D. L. Dexter, Phys. Rev. **83**, 435 (1951).

⁵ D. L. Dexter, Phys. Rev. **108**, 707 (1957).

⁶ T. Muto and H. Okuno, J. Phys. Soc. Japan **11**, 633 (1956).

⁷ T. Muto, S. Oyama, and H. Okuno, Progr. Theoret. Phys. (Kyoto) **20**, 804 (1958).

⁸ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

⁹ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).

if the transfer mechanism is to yield sensible results, the transfer function must be either more localized than the free atom Na 3s function or have an oscillating tail which tends to reduce the overlap and exchange effects.

These results leave open for criticism the consequences of Overhauser's³ analysis; namely, that the fundamental band of an fcc crystal should consist of a multiplet of five lines, while that of a bcc crystal should consist of six lines. However, in his development it is necessary only that the excited one-electron wave functions located about the hole transform into each other under the symmetry operations of the cubic group. This leaves considerable freedom for the selection of the one-electron transfer function. Proceeding, therefore, on the premise that transfer is the primary mechanism involved in the absorption process, the model has been investigated in the following approximations.

In Sec. III, the problem of total oscillator strength associated with the five exciton lines predicted for an fcc crystal is discussed. Using the free atom Na 3s function for the transfer function and including its overlap with the nearest neighbor Cl⁻ 3p and 3s functions as well as overlap between nearest and next nearest neighbor Na 3s functions, an oscillator strength of 5.2 is computed for NaCl. In view of the preceding results, the disparity between this value and the experimental value of about 1^{10,11} is not surprising.

In Sec. IV, a semiquantitative study of chloride, bromide, and iodide structure is made by neglecting all overlap and exchange effects except those associated with the excited electron and its nearest neighbor outer p shells. The overlap, α , between the transfer function and its nearest neighbor outer shell functions is treated as a parameter in the sense that all Coulomb and exchange interactions involving overlaps of the transfer function with neighboring p electrons are assumed proportional to α ; the proportionality constant being determined from the results obtained using the free atom Na 3s function and the chlorine ion 3p functions. Experimental values for the spin-orbit splitting of the ground-state configuration of the halogen atoms are used in conjunction with the spin-orbit term of the Hamiltonian. The polarization correction is assumed to be a multiple of the unit matrix, and therefore does not contribute to structure. Within the limits of these approximations and choosing $\alpha=0.1$, agreement is found for the doublet structure observed in the chlorides, bromides, and iodides. For NaCl this choice of α yields an oscillator strength of 0.8.

II. ELEMENTARY TRANSFER PROCESS

Consider a localized excitation in cell L of a NaCl crystal having N unit cells. The excited electron can be localized on any one of the six nearest neighbor Na⁺

ions and may have either (+) or (-) spin. These will be represented by $x_L^\pm, \bar{x}_L^\pm, y_L^\pm, \bar{y}_L^\pm, z_L^\pm, \bar{z}_L^\pm$ where the barred and unbarred quantities are on opposite sides of the Cl⁻ ion, the superscripts denote spin, and the subscript L denotes unit cell location of the hole. The one-electron functions appearing in the ground-state wave function of the crystal will be designated by ν . The Cl⁻ 3p functions (taken to be polarized along the cubic axes) at cell L will be denoted by $\tilde{x}_L^\pm, \tilde{y}_L^\pm, \tilde{z}_L^\pm$. The Cl⁻ 3s functions at cell L will be denoted by \tilde{s}_L^\pm .

Suppose that the electron occupying the \tilde{y}_L^+ state is excited to an x_L^+ state. The crystal wave function corresponding to this excitation will be written as

$$\Phi = B' x_L^+(1) y_L^-(2), \quad (2.1)$$

where

$$B' = A / (28N!)^{\frac{1}{2}}, \quad (2.2)$$

$$y_L^-(2) = \tilde{y}_L^-(2) \tilde{x}_L^+(3) \tilde{x}_L^-(4) \tilde{z}_L^+(5) \times \tilde{z}_L^-(6) \prod_{\nu \neq 3PL} [\nu(r_\nu)]. \quad (2.3)$$

In the above, $\prod_{\nu \neq 3PL} \nu(r_\nu)$ represents the product of one-electron functions excluding the Cl⁻ 3p shell at cell L , and A is the antisymmetrization operator. The wave function Φ is now regarded as an approximate eigenfunction of the Hamiltonian

$$H = \sum_i H_i + \frac{1}{2} \sum_{i,k \neq i} H_{ik} + \sum_i H_i^s, \quad (2.4)$$

where

$$H_i = \frac{p_i^2}{2m} - e^2 \sum_G \frac{Z_G}{r_{iG}}; \quad H_{ik} = \frac{e^2}{r_{ik}}; \quad H_i^s = \zeta(i) \mathbf{L}_i \cdot \mathbf{S}_i.$$

Kinetic, Coulomb, and spin-orbit energies are represented by (2.4). Ionic motion is neglected. Before writing out explicitly the inner product $\langle \Phi | H | \Phi \rangle$, it is convenient to use the Schmidt orthogonalization procedure and replace the excited electron wave function by

$$\Gamma_L^\pm = \gamma_L^\pm - \sum_\nu \langle \gamma_L^\pm | \nu \rangle \nu, \quad (2.5)$$

where

$$\gamma_L^\pm = x_L^\pm, \bar{x}_L^\pm, y_L^\pm, \bar{y}_L^\pm, z_L^\pm, \bar{z}_L^\pm.$$

Thus, (2.5) stands for

$$X_L^\pm = x_L^\pm - \sum_\nu \langle x_L^\pm | \nu \rangle \nu, \text{ etc.}$$

In our approximation, the sum in (2.5) is over those Cl⁻ 3p and Cl⁻ 3s wave functions which are centered about the six ions neighboring the neutralized alkali. We define

$$\alpha = \langle x_L^\pm | \tilde{x}_L^\pm \rangle, \quad (2.6)$$

$$\beta = \langle x_L^\pm | \tilde{s}_L^\pm \rangle. \quad (2.7)$$

Direct calculation gives $\alpha=0.219$ and $\beta=0.232$. Since the remaining overlaps are on the order of 0.05 or less, it is felt that by including the α and β overlaps we have considered (as far as exchange effects are concerned)

¹⁰ P. L. Hartman, J. R. Nelson, and J. G. Siegfried, Phys. Rev. **105**, 123 (1957).

¹¹ J. Hopfield, thesis, Cornell University, 1958 (unpublished).

the important contributions. It is to be noted that

$$\Phi = B'x_L^+y_L^- = B'X_L^+Y_L^-, \quad (2.8)$$

because of the exclusion principle. It is now a straightforward procedure to show that the energy associated with the wave function (Φ) minus the ground-state energy is

$$E = -M(\tilde{y}; \tilde{y}) + (1/\rho) \times [M(X; X) - C(X; X) + I(X; X)], \quad (2.9)$$

where

$$\rho = 1 - 6(\alpha^2 + \beta^2), \quad (2.10)$$

$$M(\eta; \eta') = \sum_{\nu} (\langle \eta^{\pm\nu} | H_{12} | \eta'^{\pm\nu} \rangle - \langle \eta^{\pm\nu} | H_{12} | \nu \eta'^{\pm} \rangle + \langle \eta^{\pm} | H_1 | \eta'^{\pm} \rangle), \quad (2.11)$$

$$C(\eta; \eta') = \langle \eta^{\pm} \tilde{y}^{\pm} | H_{12} | \eta'^{\pm} \tilde{y}^{\pm} \rangle = \langle \eta^{\pm} \tilde{y}^{\pm} | H_{12} | \eta'^{\pm} \tilde{y}^{\mp} \rangle, \quad (2.12)$$

$$I(\eta; \eta') = \langle \eta^{\pm} \tilde{y}^{\pm} | H_{12} | \tilde{y}^{\pm} \eta'^{\pm} \rangle = \langle \eta^{\pm} \tilde{y}^{\mp} | H_{12} | \tilde{y}^{\pm} \eta'^{\mp} \rangle, \quad (2.13)$$

$$\langle ab | H_{12} | cd \rangle = \int \int a^*(1) b^*(2) H_{12} c(1) d(2) d\tau_1 d\tau_2. \quad (2.14)$$

Where the asterisk denotes the complex conjugate transpose and the integrals imply integration over spatial coordinates and summation over spins. The terms in (2.9) are easily identified. Minus $M(\tilde{y}; \tilde{y})$ is the energy required to remove a Cl^- $3p$ electron from the crystal to infinity. The quantity $(1/\rho)[M(X; X) - C(X; X)]$ apart from the contributions of overlap effects, represents the energy release associated with taking the infinitely removed electron and placing it in a $3s$ state on a Na^+ site which has had one of its nearest neighbors neutralized. The term $(1/\rho)I(X; X)$ is related to the electron-hole exchange energy.

In the absence of overlap and exchange, evaluation of (2.9) gives

$$E = 10.4 \text{ ev.} \quad (2.15)$$

Evaluation with overlap and exchange included gives

$$E = 23.2 \text{ ev.} \quad (2.16)$$

The disparity between (2.15) and (2.16) has its origin in the following term which occurs in the expansion of $(1/\rho)M(X; X)$.

$$\begin{aligned} (1/\rho) \{ & -12\beta [\langle x^+ | H_1(\tilde{s}) | \tilde{s}^+ \rangle \\ & + \sum_{\nu'} (\langle x^+\nu | H_{12} | \tilde{s}^+\nu \rangle - \langle x^+\nu | H_{12} | \nu \tilde{s}^+ \rangle)] \\ & + 6\beta^2 [\langle \tilde{s}^+ | H_1(\tilde{s}) | \tilde{s}^+ \rangle + \sum_{\nu'} (\langle \tilde{s}^+\nu | H_{12} | \tilde{s}^+\nu \rangle \\ & - \langle \tilde{s}^+\nu | H_{12} | \nu \tilde{s}^+ \rangle)] \} \simeq - (6\beta^2/\rho) \langle \tilde{s}^+ | H^F | \tilde{s}^+ \rangle \\ & = 16.4 \text{ ev.} \quad (2.17) \end{aligned}$$

H^F is the Hartree-Fock operator for the Cl^- ion about which the function \tilde{s} is centered. The prime on the summation over ν signifies that the sum is to include only those functions centered about the same site as \tilde{s} and $H_1(\tilde{s})$ implies the one-electron operator associated with the nucleus G about which the function \tilde{s} is located. The term (2.17) may be regarded as the inter-

action between an exchange hole and the Cl^- ion; proximity of the hole to the Cl^- nucleus giving rise to an overwhelming repulsive energy.

To illustrate that the inordinately large energy given in (2.16) is not peculiar to the elementary transfer function Φ , we list the corresponding energies for the other elementary transfer functions which would be expected to yield energies different from Φ .

$$B'x_L^+y_L^+ \cdots 23.2 \text{ ev,}$$

$$B'x_L^+x_L^- \cdots 21.4 \text{ ev,}$$

$$B'x_L^+x_L^+ \cdots 20.4 \text{ ev.}$$

It is clear that the large energy represented by (2.16) is not peculiar to Φ . The degeneracy between $B'x_L^+y_L^-$ and $B'x_L^+y_L^+$ is accidental.

Calling (ω_e, V_e) and (ω_h, V_h) the charge density and vacuum potential associated with the electron and hole, respectively, the polarization energy released during the transfer process is estimated as follows: The electron-hole pair is assumed to be initially in a vacuum infinitely removed from the NaCl crystal which is treated as a large homogeneous isotropic dielectric (dielectric constant κ). If the electron-hole pair is now introduced into the dielectric, the resultant decrease in electrostatic energy (i.e., Coulomb interaction plus self-energies) is just the polarization correction which must be applied to (2.15) and (2.16) to account for the polarization energy released by the lattice during the absorption process. This polarization correction is

$$P = -\left(\frac{1}{2} - \frac{1}{\kappa}\right) \int (\omega_e V_e + \omega_h V_h + 2\omega_e V_h) d\tau. \quad (2.18)$$

In the absence of overlap and exchange and choosing $\kappa = 2.25$ (the high-frequency value for NaCl), the polarization correction becomes $P = -2.6$ ev. Combining this with (2.15) gives an excitation energy of 7.8 ev.

When overlap and exchange are included, the calculation of (2.18) becomes much more difficult because the normalized orbital of the excited electron has the complex form

$$\begin{aligned} \frac{X^2}{\rho} = & -\left(x^2 - 2\alpha \sum_{i=1}^3 x\theta_i + 2\alpha \sum_{i=4}^6 x\theta_i + \alpha^2 \sum_{i=1}^6 \theta_i^2 - 2\beta \sum_{i=1}^6 x\tilde{s}_i \right. \\ & \left. + \beta^2 \sum_{i=1}^6 \tilde{s}_i^2 + 2\alpha\beta \sum_{i=1}^3 \tilde{s}_i\theta_i - 2\alpha\beta \sum_{i=4}^6 \tilde{s}_i\theta_i\right), \quad (2.19) \end{aligned}$$

where θ_i represents either \tilde{x}_i , \tilde{y}_i , or \tilde{z}_i and the indices $i = 1$ to 6 label the six sites neighboring the site about which the Na $3s$ function is centered ($i = 1, 2, 3$ are taken to be the sites for which $\langle x | \theta_i \rangle = \alpha$ and $i = 4, 5, 6$ those sites for which $\langle x | \theta_i \rangle = -\alpha$). We shall make the simplifying assumption that (2.19) represents six equal charges each having the value $-(\alpha^2 + \beta^2)/\rho$, in units of the electron charge, symmetrically spaced about the charge $1/\rho$. To estimate the self-energy associated with

each of the charges $-(\alpha^2 + \beta^2)/\rho$, it is further assumed that the charge is distributed uniformly throughout a sphere of radius r_s . Finally, interactions between the charges centered about $i=1$ to 6 as well as the interaction between these charges and the charge $1/\rho$ are approximated by replacing the distributions by point charges. The polarization correction then assumes the form

$$P \simeq (10.2 + 6.7/r_s)(1/\kappa - 1), \quad (2.20)$$

where P is in electron volts and r_s is to be expressed in Bohr radii. Choosing $\kappa = \infty$, a choice which gives maximum correction, it is found that a value of $r_s \simeq 1.3$ Bohr radii is necessary to bring (2.16) into agreement with experiment. Now the self-energies of the individual charge distributions contributing to the charge situated about each of the sites $i=1$ to 6 have been determined along with their radii r (i.e., r as determined by assuming the charge is uniformly distributed throughout a sphere). These radii are listed below:

Charge density	r (Bohr radii)
$(1/\rho)\alpha^2\bar{x}\bar{x}$	2.49
$(1/\rho)\beta^2\bar{s}\bar{s}$	2.16
$(1/\rho)2\alpha x\bar{x}$	2.61
$(1/\rho)2\beta x\bar{s}$	3.06

These calculations indicate that the charge distributions contributing to the charge situated about each of the sites $i=1$ to 6 are not sufficiently localized to make the value of $r \simeq 1.3$ seem reasonable. Moreover, if a more palatable choice of κ were used, such as $\kappa = 2.25$, a totally unreasonable value of $r_s \simeq 0.4$ is necessary to bring (2.16) into agreement with experiment. A reasonable value of r_s would appear to be $\simeq 2.5$. Using this figure and taking $\kappa = 2.25$ gives an excitation energy of 16 ev. It must be concluded, therefore, that the simple electron transfer model in which the excited electron function is taken to be the free atom Na 3s electron leads to results which are irreconcilable with experiment. This conclusion is corroborated by the oscillator strength calculation given in the following section.

III. OSCILLATOR STRENGTHS

Defining $B = A/[(28N!)^{1/2}N^{1/2}]$ and ρ_n ($n=1-5$) to be the normalizing constants, the five exciton functions Ψ_n formulated by Overhauser³ may be written as follows:

$$\Psi_1 = \frac{B}{(12\rho_1)^{1/2}} \sum_L (s_L^+ y_L^- - s_L^- y_L^+), \quad (3.1)$$

$$\Psi_2 = \frac{B}{2(6\rho_2)^{1/2}} \sum_L (t_L^+ y_L^- - t_L^- y_L^+), \quad (3.2)$$

$$\Psi_3 = \frac{B}{2(6\rho_3)^{1/2}} \sum_L (s_L^+ x_L^- + s_L^- x_L^+ + s_L^+ \bar{s}_L^- - s_L^- \bar{s}_L^-), \quad (3.3)$$

$$\Psi_4 = \frac{B}{4(3\rho_4)^{1/2}} \sum_L (u_L^+ x_L^- + u_L^- x_L^+ + v_L^+ \bar{s}_L^- - v_L^- \bar{s}_L^-), \quad (3.4)$$

$$\Psi_5 = \frac{B}{4(\rho_5)^{1/2}} \sum_L (w_L^+ x_L^- + w_L^- x_L^+ + r_L^+ \bar{s}_L^- - r_L^- \bar{s}_L^-), \quad (3.5)$$

where

$$r = (y + \bar{y}) - (x + \bar{x}), \quad (3.6)$$

$$s = (x + \bar{x} + y + \bar{y} + z + \bar{z}), \quad (3.7)$$

$$t = 2(y + \bar{y}) - (z + \bar{z} + x + \bar{x}), \quad (3.8)$$

$$u = 2(x + \bar{x}) - (y + \bar{y} + \bar{z} + z), \quad (3.9)$$

$$v = 2(z + \bar{z}) - (x + \bar{x} + y + \bar{y}), \quad (3.10)$$

$$w = (y + \bar{y}) - (z + \bar{z}). \quad (3.11)$$

A quantitative study of structure requires finding those linear combinations of (3.1) through (3.5) which diagonalize H . However, the total oscillator strength associated with the five exciton lines can be computed without knowledge of the eigenstates. The total oscillator strength associated with the five exciton states is

$$f = \frac{2m}{\hbar^2} \sum_{\lambda=1}^5 E^0 \left| \left\langle \sum_{n=1}^5 a_n^\lambda \Psi_n \right| \sum_i \mathbf{r}_i \right| \Psi_0 \rangle \right|^2. \quad (3.12)$$

Here, Ψ_0 is the ground-state wave function of the crystal, $\sum_n a_n^\lambda \Psi_n$ is the eigenfunction of H corresponding to the eigenvalue E^λ , and E^0 is the energy difference between the energy E^λ and the ground-state energy. The energy E^0 is taken to be 7.7 ev for each of the exciton lines. In addition to including the α and β overlaps, we shall also include in the calculation the overlaps

$$\begin{aligned} \delta &= \langle x | y \rangle \\ \gamma &= \langle x | \bar{x} \rangle \end{aligned} \quad (3.13)$$

Direct calculation gives $\delta = 0.359$ and $\gamma = 0.144$. Using (3.1) through (3.5) it can be shown that for the overlaps considered

$$\mathbf{M}_1 = \langle \Psi_1 | \sum_i \mathbf{r}_i | \Psi_0 \rangle = \frac{N^{1/2}}{(12\rho_1)^{1/2}} [4Q_1 + 8Q_2] \mathbf{u}, \quad (3.14)$$

$$\mathbf{M}_2 = \langle \Psi_2 | \sum_i \mathbf{r}_i | \Psi_0 \rangle = \frac{N^{1/2}}{(24\rho_2)^{1/2}} [8Q_1 - 8Q_2] \mathbf{u}, \quad (3.15)$$

$$\mathbf{M}_n = \langle \Psi_n | \sum_i \mathbf{r}_i | \Psi_0 \rangle = 0 \quad n=3, 4, 5, \quad (3.16)$$

$$Q_1 = \langle y | \mathbf{r} \cdot \mathbf{u} | \bar{y} \rangle - \beta \langle \bar{s} | \mathbf{r} \cdot \mathbf{u} | \bar{y} \rangle, \quad (3.17)$$

$$Q_2 = \langle x | \mathbf{r} \cdot \mathbf{u} | \bar{y} \rangle - \beta \langle \bar{s} | \mathbf{r} \cdot \mathbf{u} | \bar{y} \rangle, \quad (3.18)$$

$$\begin{aligned} \rho_1 &= 1 + 4\delta + \gamma - 5\alpha^2 - 15\beta^2; \\ \rho_2 &= 1 - 2\delta - 5\alpha^2 - 3\beta^2. \end{aligned} \quad (3.19)$$

In the above, \mathbf{u} is a unit vector in the y direction. Using (3.14), (3.15), and (3.16), it is a simple matter to

reduce (3.12) to the form

$$\frac{f}{N} = \frac{8mE}{3\hbar^2} \left[\frac{(Q_1 + 2Q_2)^2}{\rho_1} + \frac{2(Q_1 - Q_2)^2}{\rho_2} \right]. \quad (3.20)$$

Direct evaluation gives

$$\rho_1 = 1.53, \quad \rho_2 = 0.025, \quad (3.21)$$

$$Q_1 = +0.604, \quad Q_2 = +0.334. \quad (3.22)$$

Inserting these values in (3.20), we obtain the value 5.2 for the total oscillator strength per unit cell. This is in gross disagreement with the experimental value of $\simeq 1$.

Taking the transfer function equal to the free atom Na 3s function and including the δ , γ overlaps, Dexter⁵ has calculated the total oscillator strength associated with the exciton lines to be 1.585. The discrepancy between this value and the present value of 5.2 is due in part to the effect of the α , β overlaps on the normalization constants ρ_1 and ρ_2 and in part to the effect of the β overlap on the matrix elements Q_1 and Q_2 . While Dexter's value for the total oscillator strength leaves open to question the applicability of the free atom Na 3s function as the transfer function, the present value demonstrates quite conclusively its inadequacy.

IV. STRUCTURE

We now find the linear combinations of (3.1) through (3.5) which diagonalize the Hamiltonian given in (2.4). Such combinations will be an improvement on the simple electron transfer functions investigated in Sec. II because they incorporate the symmetry demands of the lattice and satisfy as well the requirements for an optical dipole transition from the crystal ground state. However, they will at best still be approximate solutions, since a one-electron approximation is made. We write

$$H \sum_n a_n^\lambda \Psi_n = E^\lambda \sum_n a_n^\lambda \Psi_n. \quad (4.1)$$

Taking the inner product of (4.1) with Ψ_m yields

$$\sum_n (H_{mn} - E^\lambda \rho_{mn}) a_n^\lambda = 0, \quad (4.2)$$

where H_{mn} are the matrix elements of H in the space defined by the functions (3.1) through (3.5). This is a secular equation of order five which will yield five eigenvalues and five associated eigenvectors. Writing

$$H' = \sum_i H_i + \frac{1}{2} \sum_{i, k \neq i} H_{ik}, \quad (4.3)$$

the matrix elements of H' are most easily derived by replacing x by X , y by Y , etc. (where X , Y , etc., are defined in 2.5), in (3.6) through (3.11). This substitution does not alter the wave functions (3.1) through (3.5) because of the exclusion principle and because it is only the combinations $(x+\bar{x})$, $(y+\bar{y})$, and $(z+\bar{z})$

which occur. The matrix elements H_{mn}' are listed below.

$$\begin{aligned} H_{11}' = & G - M(\bar{y}; \bar{y}) + (1/\rho_1) [\frac{1}{2}M(X+\bar{X}; X+\bar{X}) \\ & + 4M(X; Y) - \frac{1}{3}C(X+\bar{X}; X+\bar{X}) \\ & - \frac{1}{6}C(Y+\bar{Y}; Y+\bar{Y}) - (8/3)C(X; Y) - \frac{4}{3}C(X; Z) \\ & + \frac{2}{3}I(X+\bar{X}; X+\bar{X}) + \frac{1}{3}I(Y+\bar{Y}; Y+\bar{Y}) \\ & + (16/3)I(X; Y) + (8/3)I(X; Z) + \frac{1}{3}D_1], \quad (4.4) \end{aligned}$$

$$\begin{aligned} H_{22}' = & G - M(\bar{y}; \bar{y}) + (1/\rho_2) [\frac{1}{2}M(X+\bar{X}; X+\bar{X}) \\ & - 2M(X; Y) - \frac{1}{6}C(X+\bar{X}; X+\bar{X}) \\ & - \frac{1}{3}C(Y+\bar{Y}; Y+\bar{Y}) + (8/3)C(X; Y) - \frac{2}{3}C(X; Z) \\ & + \frac{1}{3}I(X+\bar{X}; X+\bar{X}) + \frac{2}{3}I(Y+\bar{Y}; Y+\bar{Y}) \\ & - (16/3)I(X; Y) + \frac{4}{3}I(X; Z) + \frac{2}{3}D_2 \\ & - \frac{2}{3}D_3 + \frac{1}{6}D_4], \quad (4.5) \end{aligned}$$

$$\begin{aligned} H_{33}' = & G - M(\bar{y}; \bar{y}) + (1/\rho_1) [\frac{1}{2}M(X+\bar{X}; X+\bar{X}) \\ & + 4M(X; Y) - \frac{1}{3}C(X+\bar{X}; X+\bar{X}) \\ & - \frac{1}{6}C(Y+\bar{Y}; Y+\bar{Y}) - (8/3)C(X; Y) \\ & - \frac{4}{3}C(X; Z)], \quad (4.6) \end{aligned}$$

$$\begin{aligned} H_{44}' = & G - M(\bar{y}; \bar{y}) + (1/\rho_2) [\frac{1}{2}M(X+\bar{X}; X+\bar{X}) \\ & - 2M(X; Y) - \frac{1}{6}C(X+\bar{X}; X+\bar{X}) \\ & - \frac{1}{3}C(Y+\bar{Y}; Y+\bar{Y}) + (8/3)C(X; Y) \\ & - \frac{2}{3}C(X; Z)], \quad (4.7) \end{aligned}$$

$$\begin{aligned} H_{55}' = & G - M(\bar{y}; \bar{y}) + (1/\rho_2) [\frac{1}{2}M(X+\bar{X}; X+\bar{X}) \\ & - 2M(X; Y) - \frac{1}{2}C(X+\bar{X}; X+\bar{X}) \\ & + 2C(X; Z)], \quad (4.8) \end{aligned}$$

$$\begin{aligned} H_{12}' = H_{21}' = & [1/(2\rho_1\rho_2)^{\frac{1}{2}}] [\frac{1}{3}C(X+\bar{X}; X+\bar{X}) \\ & - \frac{1}{3}C(Y+\bar{Y}; Y+\bar{Y}) - \frac{4}{3}C(X; Y) + \frac{4}{3}C(X; Z) \\ & - \frac{2}{3}I(X+\bar{X}; X+\bar{X}) + \frac{2}{3}I(Y+\bar{Y}; Y+\bar{Y}) \\ & + (8/3)I(X; Y) - (8/3)I(X; Z) + \frac{2}{3}D_2 \\ & + \frac{1}{3}D_3 - \frac{1}{3}D_4], \quad (4.9) \end{aligned}$$

$$\begin{aligned} H_{34}' = H_{43}' = & [1/(2\rho_1\rho_2)^{\frac{1}{2}}] [\frac{1}{3}C(X+\bar{X}; X+\bar{X}) \\ & - \frac{1}{3}C(Y+\bar{Y}; Y+\bar{Y}) - \frac{4}{3}C(X; Y) \\ & + C(X; Z)]. \quad (4.10) \end{aligned}$$

In the above, G is the ground-state energy of the crystal, $M(\eta, \eta')$, $C(\eta, \eta')$, and $I(\eta, \eta')$ are given in (2.11), (2.12), and (2.13), respectively; ρ_1 and ρ_2 are given in (3.19). Also

$$\begin{aligned} D_1 = & \sum_{L \neq 0} \exp(i\mathbf{K} \cdot \mathbf{L}) \langle (X_0 + \bar{X}_0 + Y_0 + \bar{Y}_0 + Z_0 + \bar{Z}_0) \bar{y}_L \\ & \times |H_{12}| \bar{y}_0(X_L + \bar{X}_L + Y_L + \bar{Y}_L + Z_L + \bar{Z}_L) \rangle \quad (4.11) \end{aligned}$$

$$\begin{aligned} D_2 = & \sum_{L \neq 0} \exp(i\mathbf{K} \cdot \mathbf{L}) \langle (Y_0 + \bar{Y}_0) \bar{y}_L \\ & \times |H_{12}| \bar{y}_0(Y_L + \bar{Y}_L) \rangle, \quad (4.12) \end{aligned}$$

$$\begin{aligned} D_3 = & \sum_{L \neq 0} \exp(i\mathbf{K} \cdot \mathbf{L}) \langle (Y_0 + \bar{Y}_0) \bar{y}_L \\ & \times |H_{12}| \bar{y}_0(X_L + \bar{X}_L + Z_L + \bar{Z}_L) \rangle, \quad (4.13) \end{aligned}$$

$$\begin{aligned} D_4 = & \sum_{L \neq 0} \exp(i\mathbf{K} \cdot \mathbf{L}) \langle (X_0 + \bar{X}_0 + Z_0 + \bar{Z}_0) \bar{y}_L \\ & \times |H_{12}| \bar{y}_0(X_L + \bar{X}_L + Z_L + \bar{Z}_L) \rangle. \quad (4.14) \end{aligned}$$

The terms (4.11) through (4.14) occur because the wave functions are excitons. Here it is necessary to retain the phase factor $\exp(i\mathbf{K}\cdot\mathbf{L})$ (\mathbf{K} equal the photon wave number) since these terms represent dipole-dipole interactions which in the absence of a phase factor would be volume dependent. We have used the results of Heller and Marcus¹² to evaluate these dipole-dipole interactions and have assumed K to be normal to the dipole moment associated with the charge overlaps which occur in the terms D_1 , D_2 , D_3 , and D_4 (i.e., transverse excitons have been assumed).

The matrix $[\rho_{mn}]$ is readily shown to be equal to the unit matrix. Finally, the spin-orbit matrix given below has been derived by Overhauser.³

$$[\langle\Psi_m|\sum_i H_i^s|\Psi_n\rangle] = -\frac{\lambda}{6} \begin{pmatrix} 0 & 0 & 2\sqrt{2}i & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{2}i & 6\frac{1}{2}i \\ -2\sqrt{2}i & 0 & 2 & 0 & 0 \\ 0 & \sqrt{2}i & 0 & -1 & -\sqrt{3} \\ 0 & 6\frac{1}{2}i & 0 & -\sqrt{3} & 1 \end{pmatrix}. \quad (4.15)$$

Here λ is the spin-orbit splitting parameter of the ground-state configuration of the halogen atom. These results for the matrix elements H_{mn} , as well as the re-

sult of the unit matrix property of $[\rho_{mn}]$ could be used in a calculation which included the four major overlaps (α , β , γ , and δ) and their associated exchange effects. However, it is clear from the results of Secs. II and III that such a calculation would yield absurd results if the free atom Na 3s function were used for the transfer function. We will investigate the structure assuming that it is only the overlap of the excited electron with its nearest neighbor outer p shells which is important. We shall also assume that the "jump" frequency of the excited electron about the hole is of the same order of magnitude as the frequencies of the atomic electrons so that they will be able to follow the motion of the excited electron. We also assume that the exciton propagates so rapidly that the ions cannot follow the disturbance. The polarization correction then becomes a multiple of the unit matrix and does not contribute to structure. The overlap α between the excited electron function and its nearest neighbor outer shell p functions is treated as a parameter in the sense that all Coulomb and exchange interactions involving overlaps of the transfer function with neighboring p electrons are assumed proportional to α ; the proportionality constant being determined from the calculations performed in establishing the results of Sec. II. Within the limits of these approximations the only dependence on lattice parameter (as far as exciton structure is concerned) enters into the matrix elements H' through the combination $[C(Y; Y) - C(X; X)]$ which can be shown to a good approximation to vary as $1/a_0^3$ (a_0 being the

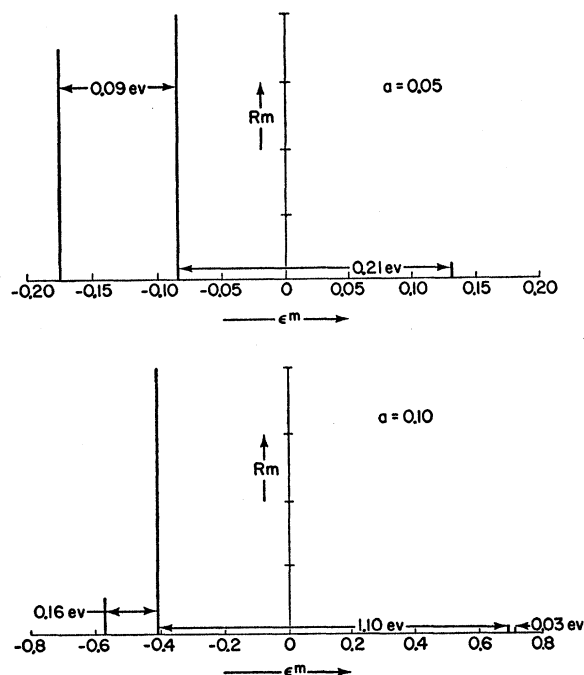


FIG. 1. Relative intensity, R_m , of the alkali chloride exciton lines and their energy separations, ϵ_m , plotted for values of the overlap integral, α , equal to 0.05 and 0.10.

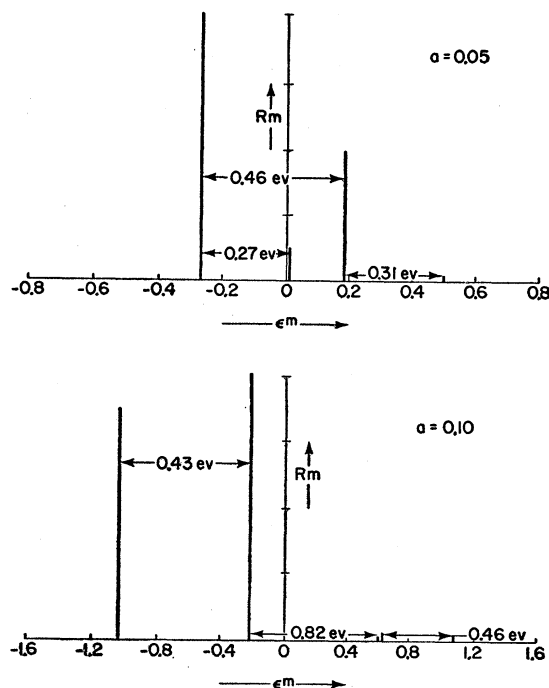


FIG. 2. Relative intensity, R_m , of the alkali bromide exciton lines and their energy separations, ϵ_m , plotted for values of the overlap integral α , equal to 0.05 and 0.10.

¹² W. R. Heller and A. Marcus, Phys. Rev. 84, 809 (1951).

lattice constant). The difference $[C(Y; Y) - C(X; X)]$ for an average bromide and iodide can then be inferred from the results for the NaCl lattice (for which the difference equals 0.06 ev). Inserting the spin-orbit splitting parameter for Cl, Br, and I in (4.15), the secular equation (4.2) has been solved for $\alpha=0.05$ and $\alpha=0.10$. The results are shown in Figs. 1 through 3. The ordinate R_m , a measure of line intensity, is defined as follows: From (3.14), (3.15), and (3.16) and recalling that in the present case $\rho_1=\rho_2$, the square of the dipole matrix element connecting the λ th eigenstate and the ground state is readily found to equal

$$|M^\lambda|^2 = (4N/3\rho_1) [(Q_1 + 2Q_2)a_1^\lambda + (2)^{1/2}(Q_1 - Q_2)a_2^\lambda]^2. \quad (4.16)$$

In the present case Q_1 and Q_2 are calculated from (3.17) and (3.18) to be

$$Q_1 = \langle y | \mathbf{r} \cdot \mathbf{u} | \bar{y} \rangle = 0.832, \quad (4.17)$$

$$Q_2 = \langle x | \mathbf{r} \cdot \mathbf{u} | \bar{y} \rangle = 0.562. \quad (4.18)$$

Inserting these values in (4.16) gives

$$|M^\lambda|^2 = (4N/3\rho_1) |1.96a_1^\lambda + 0.382a_2^\lambda|^2. \quad (4.19)$$

We have taken the quantity $R_m = |1.96a_1^m + 0.382a_2^m|^2$ as a reasonable measure of relative intensity and this is plotted as the ordinate in Figs. 1 through 3.

For $\alpha=0.05$, Fig. 1 shows two intense lines separated by 0.09 ev, the higher energy line being the more intense. The case $\alpha=0.10$ shows the two lines separated

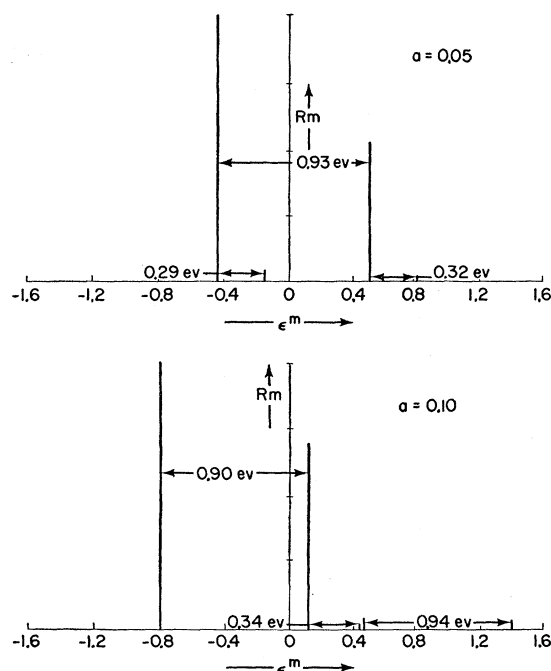


FIG. 3. Relative intensity, R_m , of the alkali iodide exciton lines and their energy separations, ϵ^m , plotted for values of the overlap integral, α , equal to 0.05 and 0.10.

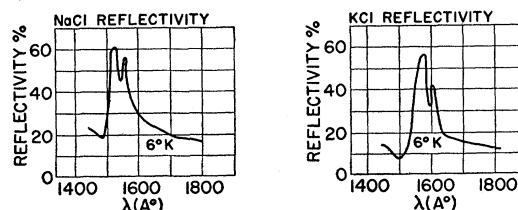


FIG. 4. Hartman's Nelson's, and Siegfried's low-temperature reflectivity measurements for NaCl and KCl.

by 0.16 ev and the ratio of intensity of the higher energy line to the lower to be 8:1. In both cases there are less intense higher energy lines. The feature of two relatively intense lines separated by the spin-orbit splitting of Cl agrees with the results of Hartman et al.,¹⁰ shown in Fig. 4. The doublet separation as determined from their curves is 0.14 ev. Choosing $\alpha=0.10$, placing $\rho_1=\rho_2=1-5\alpha^2$ in equation (3.20) and assuming Q_1 and Q_2 to be proportional to α [the proportionality constant being determined from (4.17) and (4.18)] gives a total oscillator strength of 0.8 for NaCl which is in reasonable agreement with Hopfield's¹¹ analysis of Hartman's experimental results.

For $\alpha=0.10$ the bromide structure shown in Fig. 2 consists of two relatively intense lines separated by the spin-orbit splitting of Br which agrees with the room-temperature measurements of Hilsch and Pohl.¹³

The results shown in Fig. 3 may be compared with Martienssen's¹⁴ experimental absorption curves for the iodides shown in Fig. 5. Both cases ($\alpha=0.05$ and $\alpha=0.10$) agree reasonably well with Martienssen's results for NaI and KI. However, splitting of the high-energy component in RbI is not explained. Goodman and Oen,¹⁵ without giving details, have reported calculations of the structure for NaI and CsI to be expected on the basis of Overhauser's model. For the fcc crystal they have given a doublet structure similar to that shown in Fig. 3.

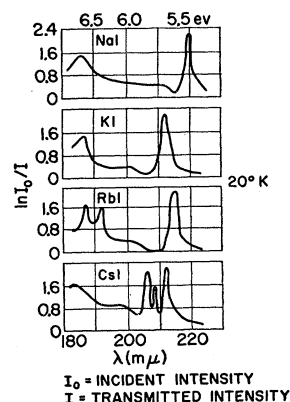


FIG. 5. Martienssen's transmission measurements for the iodides.

¹³ R. Hilsch and R. W. Pohl, Z. Physik **59**, 812 (1930).

¹⁴ W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).

¹⁵ B. Goodman and O. S. Oen, J. Phys. Chem. **8**, 291 (1959).

The rather general feature of two relatively intense lines indicated by our results may be explained on the basis of Eq. (4.19). This shows that the pure "s" state, ψ_1 , will have a dipole matrix element squared which is about 25 times that for the pure "d" state, ψ_2 . When the Coulomb and exchange matrix elements which contribute to structure are small relative to the spin-orbit matrix elements, the direct coupling between ψ_1 and ψ_3 by virtue of the spin-orbit matrix gives rise to a doublet structure separated in energy by an amount comparable to the spin-orbit coupling of the halogen ion. If, on the other hand, the Coulomb and exchange matrix elements which contribute to structure are large relative to the spin-orbit matrix elements only one intense line would be expected on the basis of Eq. (4.19). This, for example, is what is found for the chlorides if α is taken equal to 0.219.

V. CONCLUSIONS

The energy of the near ultraviolet absorption in NaCl as calculated on the basis of the elementary transfer model using the Hartree-Fock free atom Na 3s function for the transfer function is irreconcilable with experiment. The total oscillator strength, as determined using the exciton functions formulated by Overhauser³ in conjunction with the undistorted Na 3s function for the transfer function is approximately five times the experimental result.^{10,12} It must be concluded, therefore, that the undistorted free atom Na 3s function cannot be used for the one electron transfer function if the transfer model is to yield sensible results.

In a very semiquantitative way we have shown that an electron-hole overlap integral of about 0.1 yields agreement with the doublet structure observed in many of the chlorides, bromides, and iodides and a total oscillator strength in NaCl of about 0.8 which is in reasonable agreement with the experimental value of approximately one.^{10,11} It is apparent that these considerations do not distinguish the transfer model from the "excitation model."

In view of the semiquantitative nature of Secs. IV and V, it is clear that reliable results can be obtained only if the transfer function is determined in a rigorously

consistent way. This is a very complicated correlation problem, complicated not only by electronic polarization but also by lattice polarization in a way similar to the polaron problem.¹⁶ When considering the problem of line intensity, this requirement on the accuracy of the transfer function becomes even more demanding since oscillator strengths depend more sensitively on the wave function than energy. Work has been reported on a quantum mechanical calculation of the exciton peak in NaCl using the elementary transfer model.¹⁷ However, numerical details of the one electron transfer function incorporated in the calculation have not, to the author's knowledge, been published.

In carrying out the calculations of the foregoing sections, extensive use has been made of the techniques developed by Löwdin.¹⁸

ACKNOWLEDGMENTS

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Note added in proof. Since the completion of this work two particularly relevant papers have appeared:

(i) R. S. Knox and M. Inchauspé¹⁹ discuss similar aspects of the "excitation" and "charge transfer" models.

(ii) Eby, Teegarden, and Dutton²⁰ give measured absorption spectra of the alkali halides, with the exception of LiF, at room temperature and 80°K in the region from 1100 Å to 2500 Å.

¹⁶ H. Haken, Z. Physik **147**, 323 (1957).

¹⁷ I. M. Dykman and A. A. Tsertsvadze, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 1319 (1958) [translation: Soviet Phys.-JETP **34**(7), 910 (1958)].

¹⁸ Per-Olov Löwdin, *Some Properties of Ionic Crystals* (Almqvist and Boktryckeri AB, Uppsala, 1948).

¹⁹ R. S. Knox and M. Inchauspé, Phys. Rev. **116**, 1093 (1960).

²⁰ J. E. Eby, R. J. Teegarden, and D. R. Dutton, Phys. Rev. **116**, 1099 (1960).