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Exciton Models in the Alkali Halides*

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The common models for excitons in the alkali halides are criticized as to their goodness as zero-order models. Some new calculations on energies, oscillator strengths, and charge distributions are made with the models as they are commonly used. It is shown that the customary use of an LCAO (linear combination of atomic orbitals) method with the electron-transfer model gives qualitatively incorrect results, particularly for the wave functions and charge distributions, results which are not even internally consistent with the model. It is argued that the other model, an excitation model, gives at least semiquantitatively correct results, and is a satisfactory zero-order approximation. Finally, it is shown that in the alkali halides the LCAO method must inevitably be an inconvenient one for finding accurate charge distributions and wave functions for localized centers.

CONSIDERABLE work has been done in recent years on the theory of excitons in the alkali-halide crystals. This work has been based implicitly or, usually, explicitly on either of two general models, which may be labeled the electron-transfer model and the excitation model. It should perhaps be emphasized that both models are really "zero-order" approximations. Suitable modifications of either one could in principle lead to accuracy as great as one would wish. It is the purpose of this note to investigate some of the implications of these models as they are commonly (and can be easily) used, not to discuss the rapidity of the convergence of each to an exact treatment.

DESCRIPTION OF THE MODELS

The excitation states of interest are the excited, nonconducting states of the whole system. Because of the equivalence of the many unit cells, these states are described by momentum eigenfunctions, and the term "exciton" originally[1] emphasized the free-particle-like aspect of the excitation and the coherence of the wave; i.e., the true exciton is a quantum of electronic excitation energy characterized by a single propagation vector. Hence an (unnormalized, zero-order) exciton wave function may be written in the form

$$\Phi_n^{\mathbf{k}}(\mathbf{r})=\sum_J \Psi_n^J(\mathbf{r}-\mathbf{R}_J)e^{i\mathbf{k}\cdot\mathbf{R}_J}, \tag{1}$$

where the summation is over all the unit cells of the crystal characterized by the fiducial vectors $\mathbf{R}_J$, where $\hbar\mathbf{k}$ is the momentum of the exciton, and where Ψ_n^J is the nth excited state localized about the Jth cell.[2] Thus the wave function is a perfectly coherent sum of localized states, with a phase factor given by the propagation vector $\mathbf{k}$. Momentum selection rules forbid optical transitions to most of the exciton states in a mathematically perfect crystal, but of course deviations from perfect periodicity break down these selection rules, and allow absorption bands rather than discrete lines.

Theoretical work on the properties of excitons has largely been based on a very much oversimplified model, in which surface effects, internal deviations from periodicity, and the attenuation of the incident light beam have not been adequately considered. In order that the excited state approximate a true exciton state, the region of coherence must be large with respect to the wavelength of the exciton. Thus it seems extremely improbable that in the alkali halides such an object as the exciton ever exists in its traditional form, since (a) the electric dipole associated with it is readily scattered by the charged lattice vibrations and static imperfections, giving a scattering length (hence a coherent region) no greater than a few lattice constants, and (b) the reciprocal absorption coefficient is less than one hundred lattice constants, again reducing the possible coherent region. It is possible, in fact, that a better approximation to the excited states in alkali halides is to neglect the coherence essential to the exciton concept, and to consider the excitation energy as jumping almost randomly from one halide ion to a neighbor. In any event, one must in practice consider exciton wave packets of greater or lesser extent. The term exciton is sometimes loosely applied to *any* quantum of electronic excitation energy, regardless of the degree of coherence or of the nearness to being in a momentum state. This confusion in the meaning of the term seems to the writer an unfortunate one, since important aspects depend on the coherence of the true exciton.

This problem, however, need not concern us here in great detail. The two models with which we have to deal are connected with the choice of the localized eigenfunctions Ψ_n^J in Eq. (1), of which excitons, or exciton packets, are constructed.

(a) Electron-Transfer Model

The most commonly used model in the alkali halides, emphasized in the work of von Hippel,[3] involves the

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[1] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931); Physik Z. Sowjetunion **9**, 158 (1936); R. Peierls, Ann. Physik **13**, 905 (1932).

[2] D. L. Dexter and W. R. Heller, Phys. Rev. **91**, 273 (1953), and references to earlier work contained therein.

[3] A. von Hippel, Z. Physik **101**, 680 (1936).

transfer of an electron from a halide ion to the nearest alkali ions. The lowest energy excited state would then consist of a halogen atom surrounded by six alkali ions sharing symmetrically one electron.[4] This model has been used to compute the energy of the excited state,[3] as discussed below, and gives fair agreement with experiment. It has also been used in a group-theoretical analysis by Overhauser to compute qualitatively the fine structure which might occur in the absorption bands associated with transitions to the exciton states.[5] Bassani and Inchauspé have likewise used the model recently in a computation of the energies of the α and β bands in the alkali halides.[6]

(b) Excitation Model

In the alternative model, emphasis is given to the interaction between the excited electron and the Madelung potential at the halide-ion site.[7] Thus the lowest excited state in this model consists of an electron in a partially s-like state bound to the Madelung well, such that within the well the electron's wave function looks similar to that of an excited halogen atom, and outside the well like a conduction-band wave function modified by an envelope function arising from the attraction by the Madelung well. A more precise description appears in the next section.

ENERGY

Several measurable quantities can be computed on the basis of these models. The energy of the transition corresponding to the first fundamental absorption band is perhaps the first which one would attempt.

(a) Electron-Transfer Model

Following von Hippel,[3,8] we may compute a zero-order value for the energy by a simple cycle. This procedure results in an energy which is too high by between 3 and 4 ev, e.g., in NaCl 11.3 ev rather than the observed 7.7 ev. By making a number of corrections, some of which are questionable, it has been possible to bring the computed value to within about one-half ev of the observed value.

(b) Excitation Model

With this model the energy of the first fundamental absorption band can easily be computed by (1) calculating the energy of the exciton state with respect to the bottom of the conduction band, (2) calculating the photoconductive threshold, and (3) subtracting. Mott and Littleton[9] have computed the position of the valence band (assumed narrow) with respect to the vacuum levels with the use of another cycle and a calculated polarization energy. For NaCl this value was 10.2 ev. Tibbs[10] has attempted to compute the electron affinity of NaCl, but was able to conclude only that it is small. An experiment by Gyulai,[11] comparing the photoelectric thresholds of Na in vacuum and in NaCl, indicates an electron affinity of about 0.5 ev. Thus, we may take 9.7 ev as the energy gap between valence and conduction bands.

The energy of the lowest exciton state with respect to the conduction band may be estimated crudely on the basis of the model of reference 7 to be $-e^2/18a_0$, or -1.5 ev, giving a first fundamental absorption-band position of 8.2 ev for NaCl. A more detailed calculation,[12] based on essentially the same model, replaces the figure -1.5 by -1.8 ev, predicting a band position of 7.9 ev. This figure is to be compared with a measured value of 7.7 ev at room temperature. Thus, this model affords a good zero-order calculation, with fewer and much smaller corrections than the other.

OSCILLATOR STRENGTHS

With these models it is also possible to predict absorption cross sections, usually a much more sensitive test of a wave function than is an energy. In order to call on earlier work we shall deal with NaCl explicitly though the results should be valid for most of the alkali halides.

(a) Electron Transfer Model

For the ground state of the localized function centered on a given Cl ion we may use the analytical approximation[7] to the Hartree $3p$ Cl^- function[13]

$$\psi_{\mathrm{Cl}}(\mathbf{r})=1.02(1.1^5/\pi)^{\frac{1}{2}}r\cos\theta(e^{-1.1r}-23.2e^{-8r}),\quad (2)$$

where r is expressed in units of $a_0=\hbar^2/me^2$. Thus, after the transition, this state will be unoccupied, i.e., occupied by a positive hole; in a treatment of fine structure in absorption we would have to treat more carefully the wave function of the hole in conjunction with that for the excited electron.

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[4] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 411.

[5] A. Overhauser, Phys. Rev. **101**, 1702 (1956).

[6] F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957).

[7] D. L. Dexter, Phys. Rev. **83**, 435 (1951). This model, based on work by Tibbs (reference 10), is similar to the Wannier treatment [G. H. Wannier, Phys. Rev. **52**, 191 (1937)], and should be comparable in accuracy in the alkali halides, both models being based on the slowness of the variation of the perturbing potential.

[8] A description of part of the calculation is given by N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948), p. 98.

[9] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938). See also reference 8, p. 80.

[10] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).

[11] Z. Gyulai, Z. Physik **35**, 411 (1926). A photoemission experiment by M. A. Gilleo [Phys. Rev. **91**, 534 (1954)] with Ag films on NaCl indicates an electron affinity of 0.4 ev. A recent experiment by W. J. Turner [Phys. Rev. **101**, 1653 (1956)] failed to confirm this result.

[12] T. Muto and H. Okuno, J. Phys. Soc. Japan **11**, 633 (1956). Professor Muto has kindly made available a copy of his paper read at the International Congress on Theoretical Physics at Seattle, September, 1956, in which additional results are presented.

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

In the zero order, the excited states in this model are linear combinations of 3s functions centered on the six nearest Na$^+$ ion sites. Each Hartree function[14] for Na may be approximated analytically by the function

$$\varphi(r)=\frac{0.993}{(4\pi)^{\frac{1}{2}}}(4.34e^{-7.25r}-1.77e^{-2.63r}+0.243r^2e^{-0.85r}). \quad (3)$$

If we denote by the subscripts 1 and 2 the Na ion sites on the positive and negative x axis, 3 and 4 those on the y axis, and 5 and 6 on the z axis, with the Cl ion at the origin, we may write the 6 orthogonal linear combinations of the φ's as

$$\begin{aligned}
\Psi_{\mathrm{I}}&=C_1\sum_{i=1}^{6}\varphi_i,\\
\Psi_{\mathrm{II}}&=C_2(\varphi_1-\varphi_2).\\
\Psi_{\mathrm{III}}&=C_2(\varphi_3-\varphi_4),\\
\Psi_{\mathrm{IV}}&=C_2(\varphi_5-\varphi_6),\\
\Psi_{\mathrm{V}}&=C_3(\varphi_1+\varphi_2-\varphi_3-\varphi_4),\\
\Psi_{\mathrm{VI}}&=(C_3/\sqrt{3})(\varphi_1+\varphi_2+\varphi_3+\varphi_4-2\varphi_5-2\varphi_6).
\end{aligned} \quad (4)$$

The normalization constants C_1, C_2, C_3, in the neglect of overlapping of φ_j and φ_k, are $1/\sqrt{6}$, $1/\sqrt{2}$, and $\frac{1}{2}$, respectively. It is found that such a neglect is unjustified, however, and the proper values are $1/(14.50)^{\frac{1}{2}}$, $1/(1.784)^{\frac{1}{2}}$, and $1/(1.814)^{\frac{1}{2}}$, respectively as found from the overlap integrals $\int\varphi_1\varphi_3d\tau=0.3273$ and $\int\varphi_1\varphi_2d\tau=0.1082$. In Fig. 1 we have plotted the value of the (unnormalized) function Ψ_{I} of Eqs. (4) along the (1,0,0) direction. The function should be multiplied by $C_1/(4\pi)^{\frac{1}{2}}=0.0741$ in order to normalize it. Near each of the six Na ions Ψ_{I} looks very much like an Na 3s function, and behaves fairly smoothly elsewhere.

It is apparent that if Ψ_{I}, Ψ_{II}, $\cdots$ or Ψ_{VI} in Eqs. (4) were used as a localized function $\Psi_n{}^J$ in Eq. (1), some refinements would be necessary to account for the circumstance that a given Na atom's wave function appears both in $\Psi_n{}^J$ and in $\Psi_n{}^{J+1}$. That is, $\Psi_n{}^J$ and $\Psi_n{}^{J+1}$ not only are nonorthogonal, but they are partly made up of the same functions. Thus, certain problems arise in connection with forming a coherent sum of these localized functions; however, as will be seen, more serious problems, though related ones, exist with the localized functions themselves. In the following we shall consequently be concerned only with the localized functions, bearing in mind that in this model, and to a much smaller extent in the excitation model, the overlapping of the localized functions must still be considered.

The oscillator strengths for the various transitions can be expressed in terms of the two-center matrix elements,

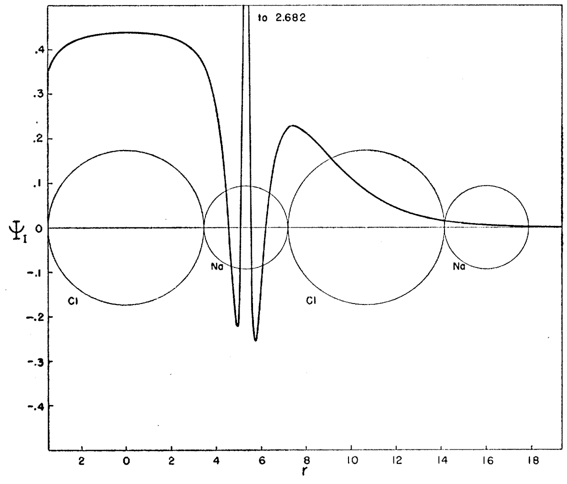

FIG. 1. Excitation model. This is a plot of the lowest energy localized excited state, Ψ_{exc} in Eq. (7) in the text, as a function of position along the (1,0,0) direction. The Cl ion at $r=0$ is the center of excitation. This function should be multiplied by 0.604 for normalization.

$$\begin{aligned}
M_1&=\int\psi_{\mathrm{Cl}}(\mathbf{r})r\cos\theta\,\varphi_1(\mathbf{r}-\mathbf{R}_1)d\tau,\\
M_3&=\int\psi_{\mathrm{Cl}}(\mathbf{r})r\cos\theta\,\varphi_3(\mathbf{r}-\mathbf{R}_3)d\tau,
\end{aligned} \quad (5)$$

which are found to be $0.872a_0$ and $0.598a_0$, respectively. The oscillator strength per Cl ion for all of the possible transitions to the states in Eqs. (4) of energy approximately E_0 is equal to

$$f=(4m/\hbar^2)E_0[4C_1^2(M_1+2M_3)^2+(16/3)C_3^2(M_1-M_3)^2]=1.585. \quad (6)$$

If we had neglected the overlapping of the Na functions, we would have obtained a total value

$$f=(4m/\hbar^2)E_0(2M_1^2+4M_3^2)=3.34,$$

so that it is clear that the overlap among the Na functions is considerable. We shall return to this aspect presently.

If absolute absorption coefficient measurements were available for the first fundamental absorption band of NaCl, we could compute the oscillator strength from the area under the absorption coefficient *versus* energy curve. This information does not seem to be available, however, and we shall have to resort to indirect methods to obtain an experimental value for f.

Mayer[15] has correlated measured relative absorption[16]

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

[15] J. Mayer, J. Chem. Phys. **1**, 270 (1933). See also reference 4, p. 658.

[16] R. Hilsch and R. W. Pohl, Z. Physik **57**, 145 (1929); **59**, 812 (1930). R. Hilsch, Z. Physik **77**, 427 (1932).

and index of refraction data[17] for NaCl, KCl, and KI, and has obtained total oscillator strengths for the halide ion in each case of 3.25, 3.24, and 4.00, respectively. It should be amphasized that these values include transitions to *all* excited bound and ionized states, not merely the ones in Eqs. (4). It is difficult to estimate accurately what fraction of the total value of 3.25 corresponds to the first fundamental band in NaCl, particularly as recent data by Hartman and co-workers[18] is not consistent with earlier work.[16,19] A fraction between $\frac{1}{5}$ and $\frac{1}{10}$ appears reasonable, however. Thus a value in the range 0.3 to 0.6 may be estimated in this way for the oscillator strength per ion for the first fundamental absorption band.

Another, probably better, method is based on an analogy with the KI system, in which absolute values have been measured for the absorption coefficient in the first fundamental absorption band.[20] From these data we obtain an integrated absorption cross section of 0.88×10^{-17} cm^2 ev for the lowest energy transition, corresponding to leaving the five valence electrons in a $j=\frac{3}{2}$ state. No really satisfactory theory exists for relating the cross section to the oscillator strength in a strongly absorbing medium,[21] but we can estimate the oscillator strength, neglecting the presence of the medium, with Eq. (27) of reference 21. With $n=1$ in Eq. (27), we find an oscillator strength of 0.093. With n equal to 1.64, the square root of the high-frequency dielectric constant, we find an oscillator strength of 0.074 for this transition. Thus we find that this transition represents a fraction (0.093/4.00) to (0.074/4), or 0.023 to 0.019 of the total oscillator strength per I^- ion. From the similarity of the relative absorption spectra among the alkali halides, we may assume that roughly the same fractional oscillator strength is associated with the same transition in NaCl, arriving at a value of 0.076 to 0.060.

In NaCl, however, the $j=\frac{3}{2}$ and $j=\frac{1}{2}$ transitions are close together, and the computations we have made in Eq. (6) with Eqs. (2) and (4) include them both. Hartman *et al.*[18] have resolved two components of which the higher energy one, presumably corresponding to the $j=\frac{1}{2}$ transition, is somewhat larger than the other, perhaps by a factor of two. (KI seems to behave similarly.) Thus the total value may be a factor of three greater than that for the $j=\frac{3}{2}$ level alone, and we obtain a value of about 0.23 to 0.18 for the total. This value of about 0.2, and the range 0.3 to 0.6 obtained from the work of Mayer and inspection of the relative absorption curves, are to be compared with the computed value in Eq. (6) of 1.585. The agreement is seen to be poor.

(b) Excitation Model

Here we may call on calculations from reference 7, in which the ground-state wave function was that of Eq. (2), and the excited-state wave function was given by

$$\Psi_{\mathrm{exc}}(\mathbf{r})=(\pi\alpha^3)^{-\frac{1}{2}}e^{-r/\alpha}g(\mathbf{r}), \tag{7}$$

with $\alpha=3$. This is a function centered about the Cl ion site, with an envelope function dropping off with a damping length of $3a_0$, and containing a periodic function $g(\mathbf{r})$, the lowest energy wave function in the conduction band. The function $g(\mathbf{r})$ has been determined for the (100) direction in NaCl by Tibbs.[10] $\Psi_{\mathrm{exc}}(\mathbf{r})$ will be discussed further in the next section. Equation (7) is plotted in Fig. 2. For normalization it should be multiplied by 0.604.

With these functions we compute[7] an oscillator strength per atom for the first fundamental absorption band,

$$f=0.4 \tag{8}$$

a value apparently in reasonable agreement with experiment.

CHARGE DISTRIBUTION

It is particularly informative in the present case to compute charge distributions with these zero-order models. As will be seen, the electron-transfer model as commonly described predicts obviously, qualitatively, incorrect results, which are not even internally consistent with the model. The excitation model, on the other hand, satisfies the intuitive conditions one would impose upon a wave function.

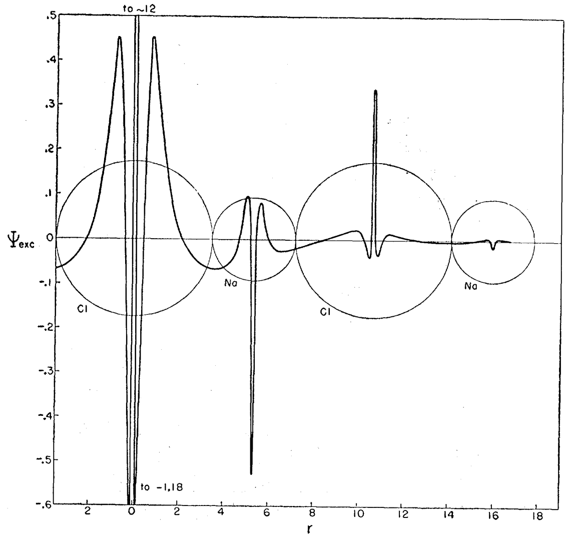

FIG. 2. Electron-transfer model. This is a plot of the lowest energy localized excited state, Ψ_{I} in Eqs. (4) in the text, as a function of position along the (1,0,0) direction. The Cl ion at $r=0$ is the center of the excitation, so that the function has cubic symmetry about $r=0$. This function should be multiplied by 0.0741 for normalization.

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[17] F. F. Martens, Ann. Physik **6**, 603 (1901); **8**, 459 (1902); Z. Gyulai, Z. Physik **46**, 80 (1928).

[18] Hartman, Nelson, and Siegfried, Phys. Rev. **105**, 123 (1957).

[19] E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937).

[20] G. Bauer, Ann. Physik **19**, 434 (1934).

[21] D. L. Dexter, Phys. Rev. **101**, 48 (1956).

(a) Electron-Transfer Model

The great spatial expanse of an alkali atom's wave function is a circumstance not generally appreciated by users of the linear combination of atomic orbitals (LCAO) method in the alkali halides. Using the wave function Ψ_{I} in Eqs. (4), we have computed the total charge on various ion sites, with the results described below. Specifically, we compute the charge contained within an "equivalent sphere" centered about the given lattice site, the equivalent sphere having a radius larger than the ionic radius by a factor 1.157 to account for the regions not contained within the ionic spheres. Thus, the equivalent sphere radii are taken to be $2.14a_0$ and $3.96a_0$ for Na and Cl, respectively.

Squaring Ψ_{I} in Eqs. (4) and integrating over the equivalent sphere, we find that 0.0108 of the charge is on each of the six Na ions whose wave function is used in the LCAO method. That is, we started by saying the electron was shared by the six Na ions, but a computation based on the model results in a conclusion that less than 7% of the electron's charge is on the six Na ions. The model clearly is far from being internally consistent when used in this way.

The charge on the central Cl ion, computed as above, is found to be 0.21 of the electron's charge. Thus, a substantial fraction of the charge is in the central sphere; indeed, almost 20 times as much is in the central Cl sphere as is in any of the six Na spheres. In this respect the model is probably qualitatively correct, but it is grossly in error in neglecting the oscillations in the wave function and charge distribution near the Cl nucleus (see Fig. 1). Since the model predicts the central Cl ion to be the most heavily populated, it should certainly take explicit account of the Pauli exclusion principle in computing the behavior of the wave function in the sphere which it predicts to be the most important. The only places where the wave function behaves qualitatively correctly are near the centers of the six nearest Na ions where there is less than 7% of the charge; the other 93% of the charge distribution is incorrectly described.

As we have seen, only 28% of the charge is on the central Cl ion and its six nearest neighbors. A large part of the remainder of the charge is predicted to be on the twelve second-nearest, the eight third-nearest, and the six fourth-nearest neighbors. In fact, there is more charge on each fourth-nearest neighbor than on each nearest neighbor.

Thus, there are two serious errors made in the predictions of this zero-order model. In the first place it predicts an extremely diffuse wave function, extending very appreciably beyond the fourth-nearest neighbors. Secondly, even if the distribution should extend out as far as predicted, which seems most unlikely, the behavior of the wave function where it is most important is completely incorrect. It is the faulty behavior on the central Cl ion which is responsible for the large oscillator strength predicted.

(b) Excitation Model

As we see in Fig. 2, the wave function based on the excitation model drops off fairly rapidly. The charge on the central Cl ion's equivalent sphere is approximately 0.75, roughly $\frac{3}{5}$ of this value coming from the lobe between $0.9a_0$ and $2.1a_0$, and most of the rest from $2.1a_0$ to $3.96a_0$. About 0.14 is contained on the six nearest Na ions, 0.09 on the twelve next-nearest neighbors, and 0.01 on the eight third-nearest neighbors. Roughly $\frac{1}{2}$ of the charge is contained within $3a_0$ and $5.32a_0$ of the central Cl ion, where $5.32a_0$ is the distance to the nearest Na ions. It is necessary to be approximate with these figures, since $g(\mathbf{r})$ has been worked out in detail only for the (1,0,0) direction; the relative errors in these figures are estimated to be less than 10%.

At least qualitatively, the wave function behaves correctly near each ion's nucleus, appearing something like a $4s$ Cl function near each Cl ion and like a $3s$ Na function near each Na ion. The wave function is not exactly correct, of course, the error being associated with the rapidly damped envelope function, but as a zero-order model it appears quite satisfactory.

FINE STRUCTURE IN ABSORPTION

A group-theoretical analysis of the fine structure to be expected with these models has been carried out recently by Overhauser.[5] He showed that with the electron-transfer model the six wave functions in Eqs. (4), combined with correct combinations of spin functions and the wave function of the positive hole left behind on the central Cl ion, could lead to five absorption lines in the first fundamental absorption band in the NaCl structure. He has further shown that the lowest energy wave function of the form Eq. (7), combined with spin functions and the wave function of the hole on the central Cl ion, can lead to two absorption lines in the first fundamental band. He concludes that fine structure in this absorption band can best be explained on the electron-transfer model, and cites data by Hartman indicating the presence of fine structure. In NaCl and KCl, Hartman and coworkers have found that "The reflectivity clearly shows the absorption to have a doubled peak at low temperatures and with a suggestion still of further possible structure on the long-wavelength side of the peak."[18]

It is possible that the LCAO method, when an adequate number of orbitals is included, may prove to be the best way of interpreting fine structure in these absorption bands, the LCAO method appearing particularly suited to the computation of symmetry properties of wave functions. As will be shown in the next section, the number of orbitals required will be inconveniently large for a self-consistent wave function, but perhaps still feasible to handle.

On the other hand, it may not be necessary to seek a difficult solution. First, the lowest energy absorption bands of the alkali iodides, where the spin-orbit interaction is large (0.94 ev), have been investigated by several groups, and seem to be simple bands. Secondly, the two lines in NaCl and KCl resolved by Hartman *et al.* have a separation of 0.12 ev and can be interpreted by the explanation of Mott and Gurney,[22] namely, the splitting of the doublet $3p^5$ configuration of the Cl atom (0.11 ev) independently of the wave function chosen for the excited electron. Thirdly, in the discussion by Overhauser of possible fine structure in absorption, no account was taken of the higher excited space states in the excitation model, whereas all six states of Eqs. (4) were considered. (In a hydrogenic approximation for the excitation model in NaCl, one would not expect higher energy absorption bands, measured from the first, for perhaps 1.3 ev. However, it is not likely that the hydrogenic approximation is a good one.) Finally, lattice vibrations can remove selection rules prohibiting some transitions in the static crystal. Thus we conclude that a simple explanation is now possible on the excitation model and may continue to be so even if additional fine structure should be discovered.[23]

LCAO METHOD IN ALKALI HALIDES

We conclude with a brief discussion of the LCAO method in the alkali halides.

This method is particularly useful, for a well-localized wave function, when the atomic orbitals are themselves small in spatial extent. If the binding of each atomic orbital to its nucleus is weak, on the other hand, a great deal of charge may be inadvertently placed in regions where it is not wanted. It is then necessary to include further orbitals with a negative coefficient, in order to remove the unwanted charge. Thus one is led to an awkward and artificial combination of atomic wave functions to achieve what is really a simple result.[24]

The alkali atomic wave functions are outstanding examples of spatially diffuse functions. Within the ionic radius of Na, 1.85 a_0, there is contained only 4.27% of the charge of a 3s Na electron. In the equivalent sphere, 2.14a_0, there is only 7.45%. Thus, it is inevitable that any LCAO containing alkali atomic functions must put a great deal of charge far from the center, necessitating the inclusion of many otherwise un-needed functions to remove most of the charge and to give oscillations to the remainder near the distant nuclei in accordance with the Pauli exclusion principle.

In the case of a center whose wave function is not well localized, one would expect to have to use many terms in the LCAO anyway, and the fact that each orbital is extensive would not necessarily be a further inconvenience (except for the number of overlap terms one would have to compute in orthogonalization and normalization). Such a case may be, for example, the excited states of an F-center in the alkali halides, or the impurity states in crystals of high dielectric constant (where one would probably not be tempted to use the LCAO method for other reasons). For the lowest exciton states and the ground states of the simple color and impurity centers in the alkali halides, on the other hand, the strong interaction between the electron and the Madelung potential well keeps the electron well localized, where, as we have seen, the expansion in terms of diffuse functions is inconvenient.[25]

Finally it should perhaps be stated explicity that our principal criticisms of the electron-transfer model relate not primarily to the physical picture, but to the existing mathematical implementation of the model; in the theoretical work based on this model the principal error seems to be related to taking too literally phrases such as "transferring an electron from a halide ion to an alkali ion," used in a qualitative description. On the excitation model, which appears to be semiquantitatively correct, almost all of the charge lies within a sphere passing through the centers of the six Na ions, a good share of it being closer to the Na nucleus than to the central Cl nucleus. Thus a qualitatively correct viewpoint is to consider the creation of the localized excited state of the Cl ion as involving the motion of an electron's charge from the Cl ion towards the Na ions. Indeed, quite a good wave function could probably be constructed from a combination of an excited Cl^- (4s) wave function and a sum of damped and highly polarized Na 3s functions. (The writer is not aware of the previous use of such a function, but it might prove to be quite useful, particularly for symmetry properties.) Wave functions constructed of linear combinations of six Na (3s) functions, as in Eqs. (4), however, cannot be considered as physically realistic.

The assistance of N. N. Axelrod, R. S. Knox, and M. P. Rimmer in programming and carrying out numerical computations is gratefully acknowledged.

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[22] See reference 8, p. 95.

[23] Muto (reference 12) discusses briefly in his Seattle paper the fine structure to be expected in absorption in the alkali halides. He has shown that several components are possible on the basis of a model similar to the excitation model treated here; further results by Professor Muto and co-workers will be forthcoming.

[24] Another technique has been utilized by Gourary and Adrian to avoid some of the difficulties associated with the use of the LCAO method for color centers in the alkali halides. [B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957); F. J. Adrian (to be published).]

[25] It has been proposed that for some computations involving the ground states of color centers in the alkali halides, a model equivalent to the excitation model described here is insufficient. Krumhansl and the writer have shown that in these cases also this model, when used correctly, is in reasonable accord with experiment. [J. A. Krumhansl, Phys. Rev. **93**, 245 (1954); D. L. Dexter, Phys. Rev. **93**, 244 (1954). See also reference 24.]