

Optical Absorption by the Alkali Halides

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(Received August 12, 1936)

The relations are investigated between three types of theory for explaining absorption of light by ionic crystals: absorption by independent atoms or ions, absorption according to Frenkel's excitation waves, and absorption according to energy bands and lattice functions, as used in the theory of metals. It is shown that each method leads to a set of unperturbed wave functions, which are related to each other by linear combinations, and that no one set is correct at the actual distance of separation in the crystal. Instead, combinations must be used, leading both to continuous absorption as in the energy bands, and to one or

two discrete lines in connection with each continuum, as in absorption by independent atoms or in excitation waves. These conclusions are compared with experiment, explaining in a general way the sharp structure observed both in the near and far ultraviolet absorption spectra of these crystals. The discussion deals throughout with the undistorted crystal, leaving out of account the new absorption bands which are known to appear in these crystals after considerable illumination, resulting from the deposition of free alkali in the crystal.

THE electronic energy levels in the alkali halides have been the subject of much study in recent years. Experimentally, Hilsch and Pohl¹ and students of Pohl have made elaborate studies of the ultraviolet absorptions of these crystals, and also of the photochemical processes resulting from the absorption of light, including blackening of the crystal by deposit of free alkali, and subsequent photoconductivity when the crystal is illuminated with visible light. More recently, Smith² and O'Bryan³ have studied the absorption of a few of the crystals further in the ultraviolet. On the theoretical side, Hilsch and Pohl¹ have proposed a simple theory giving the position of the first ultraviolet absorption edge in terms of the lattice spacing, the ionization potential of the alkali, and the electron affinity of the halogen, following an earlier and less satisfactory theory of Wolf and Herzfeld.⁴ Frenkel⁵ has discussed the general problem of the absorption of light by crystals, though without detailed application to these particular crystals. von Hippel,⁶ in a paper which is now in proof, has carried further the type of argument used by Wolf and Herzfeld, Hilsch and Pohl, coming in some particulars to results in agreement with the

present paper. Very recently Ewing and Seitz⁷ have applied to LiF, and Shockley⁸ to NaCl, the general type of theoretical analysis which has been used with success for the energy bands in metals. A number of other workers have contributed to the field, additional references being given in the paper of von Hippel.

Three different points of view are found among the references just mentioned. The first might be called the atomic method, in which excitation is supposed to be an act confined to a single atom or ion. This method makes close connections with the well-known electrostatic theory of ionic crystals, and is the simplest mathematically and the easiest to understand. It has been used by Hilsch and Pohl, Wolf and Herzfeld, and von Hippel. The second method is that of excitation waves, in which the excited electron is no longer localized on a particular atom or ion, but is allowed to wander through the crystal. This has been employed by Frenkel. Third is the method of lattice functions, in which each electron of the crystal is supposed to be in a modulated wave traveling through the crystal, as in the theory of metals. The method has been applied to insulators by Wilson⁹ and others, and is that used by Ewing and Seitz and Shockley. It is the purpose of the present paper to investigate the relationships of these three methods, and to see which is

¹ Hilsch and Pohl, *Zeits. f. Physik* **59**, 812 (1930).

² A. Smith, *Phys. Rev.* **44**, 520 (1933).

³ H. M. O'Bryan, *Phys. Rev.* **49**, 944 (1936).

⁴ Wolf and Herzfeld, *Handbuch der Physik* (1928), Vol. XX, p. 632.

⁵ J. Frenkel, *Phys. Rev.* **37**, 17 (1931); **37**, 1276 (1931); *Phys. Zeits. Sowjetunion* **9**, 158 (1936).

⁶ A. von Hippel, *Zeits. f. Physik*, in press. The writers are greatly indebted to Professor von Hippel for the privilege of seeing this paper before publication.

⁷ Ewing and Seitz, *Phys. Rev.* this issue. The writers are greatly indebted to Dr. Seitz for the privilege of seeing this paper before publication.

⁸ W. Shockley, *Phys. Rev.* this issue.

⁹ A. H. Wilson, *Proc. Roy. Soc.* **A133**, 458 (1931); **A134**, 277 (1931).

most applicable to the actual problem. If the atomic method or the method of excitation waves is supplemented by admitting polar, or ionized, states as well as states of pure atomic excitation, it is found that the three methods represent three different sets of unperturbed wave functions, of which the correct wave functions are linear combinations. The relations between the functions are exhibited, approximations to the solution of the perturbation problem are set up, and it is shown that no one of the methods correctly represents the real state of affairs, but that two types of energy level are simultaneously present, discrete levels like those of the atomic method and a continuum as with lattice functions, agreeing with the observation of continuous absorption with sharp structure.

One feature will be entirely neglected in the present discussion, the motion of the nuclei, which we shall assume to be held in their equilibrium positions. It has been pointed out by several of the writers just quoted that excitation or ionization within the crystal will change the interatomic forces, setting the nuclei into oscillation, and that after this oscillation dies down, the excited energy level will be stabilized in such a way that the electron will not return to its normal position. In the resulting distorted position of the nuclei and electrons, the absorption frequencies will be different from those for a normal crystal. These questions are closely tied up with the mobility of the excited electrons, the blackening of the crystal by exposure to light, and the electrical conductivity of crystals illuminated by the proper wave-lengths. We shall avoid all these questions of the distorted state of the excited crystal, discussing only absorption by the normal, unblackened crystal.

LATTICE ENERGY LEVELS

We begin with the method of lattice functions and energy levels, the method of Bloch. Consider a periodic lattice containing two types of ions, as an alkali halide. There are three types of energy level for an electron moving in such a potential field: for low energy, one type of wave function is concentrated around ions of one type, and has energy levels roughly like the energy levels of that ion; a second type is concentrated around ions of the second type; the third type of wave function,

found at high energy, is shared between ions of both types. In general, the electrons normally present in an alkali halide crystal are of the first two types, while the third type is met in the excited states. We consider first the normal state and the energy levels normally occupied. For example, in NaCl, which we may consider as built up of Na⁺ and Cl⁻ ions, each sodium ion contains two 1s, two 2s, and six 2p electrons, while each chlorine contains two 1s, two 2s, six 2p, two 3s and six 3p. Corresponding for instance to each level of a single sodium ion, there will be a band of levels in the crystal, containing as many discrete levels as there are sodium ions in the crystal. This band will be of zero width in energy as long as the ions are far apart, but as they are pushed together the band will broaden. Even at the actual distance of separation, however, the sodium ions are far enough apart in proportion to the size of the ions so that the broadening is comparatively small. Except for one fact, which we shall mention immediately, we could then derive the energy levels in such a lattice, as a function of lattice spacing, by taking the energy levels in the various ions at infinite separation, and assuming those to broaden somewhat as the ions became squeezed as they are in the crystal.

The fact which we have just mentioned, one which makes ionic crystals essentially different from metals, is that the ions are charged. In a metallic crystal, where each atom is electrically neutral, it is convenient to adjust the arbitrary zero of potential, at each lattice spacing, so that the tightly bound x-ray energy levels are independent of lattice spacing.¹⁰ This demands that the potential in the immediate neighborhood of each nucleus (which we can adjust at will) be independent of lattice spacing. Such an adjustment is impossible in ionic crystals, for there is a difference of potential between the positive and negative ions which is a function of the distance, so that if the potential of one type of ion is made constant, that of the other type will change with lattice spacing. The most symmetrical assumption to make in this case is that the potential in the neighborhood of a positive ion, which will be negative on account of the predominantly negative charge of its neighbors, decreases as much

¹⁰ J. C. Slater, *Rev. Mod. Phys.* **6**, 209 (1934); J. C. Slater and H. M. Krutter, *Phys. Rev.* **47**, 559 (1935).

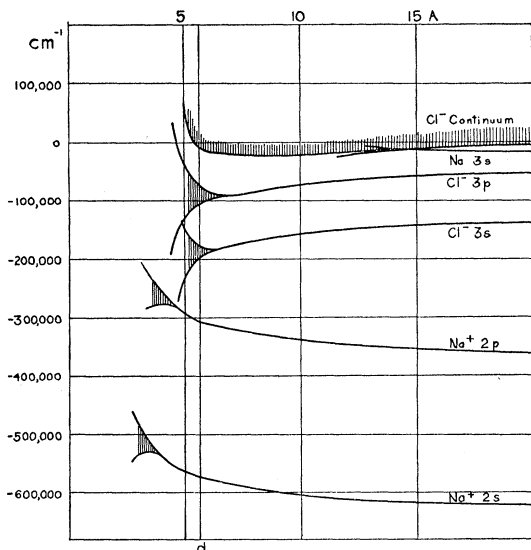


FIG. 1. One-electron energy bands in NaCl crystal.

with decreasing lattice spacing as the potential in the neighborhood of a negative ion increases. By the Coulomb law, both these variations will be inversely proportional to the lattice spacing, and we can easily get the constant of proportionality from the Madelung constant for the crystal. Thus the energy levels of an electron in this potential field will increase (on account of the negative charge of the electron) inversely proportional to the lattice spacing for those energy levels connected with positive ions, and will decrease at the same rate for negative ions, then broadening out as the ions begin to overlap, as described in the preceding paragraph.

In Fig. 1 some of these energy levels, the $2s$ and $2p$ levels of the sodium ion, the $3s$ and $3p$ of the chlorine ion, are sketched for NaCl, as a function of lattice spacing. This figure was constructed in the following manner. In the first place, the asymptotic energies were found at infinite separation from the empirical spectral terms; for the energy in a one-electron problem is an approximation to the ionization potential connected with removing the electron in question from an atom or ion. Thus the asymptotic value of $\text{Cl}^- 3p$ is taken to be the negative of the energy necessary to remove a $3p$ electron from the chlorine ion, or of the electron affinity, about $30,400 \text{ cm}^{-1}$.¹¹ The value of $\text{Cl}^- 3s$ differs from this by the energy

¹¹ Mayer and Helmholtz, *Zeits. f. Physik* 75, 29 (1932).

necessary to raise a $3s$ to a $3p$ state in neutral chlorine. (This, as a matter of fact, has not been observed; but the corresponding energy in Cl^+ is about $94,000 \text{ cm}^{-1}$, in Cl^{++} about $99,000$, and in Cl^{+++} about $103,000$, from which we may assume that in Cl it is about $89,000 \text{ cm}^{-1}$, with a probable error of perhaps 8000 cm^{-1} , or about a volt.) The asymptotic value of $\text{Na}^+ 2p$ is minus the energy required to remove a $2p$ electron from the sodium ion, and similarly for $2s$, the values being $381,000$ and $644,000 \text{ cm}^{-1}$, respectively. Knowing the asymptotic energies at infinite separations, we can then add or subtract, as the case may be, the energy $3.495 e^2/d$, where 3.495 is the appropriate Madelung number to give the electrostatic energy, d is the distance between like atoms along the axis. Expressing energies in cm^{-1} , lattice spacing in Angstroms, this becomes approximately $(405,000 \text{ cm}^{-1})/d$. The resulting lines represent the energy bands of zero width in the lattice. At small distances, we then allow these bands to be broadened in a plausible way. For the $\text{Cl}^- 3p$ band, Shockley⁸ has found the breadth at the lattice spacing of 5.63 angstroms to be approximately $35,000 \text{ cm}^{-1}$, the spreading being largely above rather than below the line derived from Madelung's constant. For $\text{Cl}^- 3s$, the overlapping of orbits is less, so that the spreading will not start until somewhat smaller lattice spacings. The sodium bands will broaden for much the same reason as in a sodium crystal, on account of the interaction of neighboring sodiums; we have accordingly assumed the same amount of broadening of these bands that there would be in the sodium crystal with the same sodium-sodium distance. Aside from these pieces of information, the pattern of the broadened bands at small distances is merely sketched in a suggestive way, not the result of calculation.

Next, we consider the excited levels. We must first notice that, though these levels can be indicated on the same diagram as the occupied ones, a different potential field must be used to determine them. Thus for an occupied level, using an argument based on the Hartree or Fock method of approximation, the ion on which the electron is found must be assumed to lack an electron by way of compensation, though the other sodium and chlorine ions have their usual single charges. For an unoccupied state, however,

it cannot be assumed that the ion on which the electron in question happens to be found lacks an electron. If we take an atomic view of the process of excitation, an electron after excitation soon travels to another ion, eventually going to quite a different part of the crystal, finding itself on ions which have their normal charges. At large distances, then, the excited sodium-like levels will approximate those of an electron in the field of a singly charged sodium ion; that is, they will be the levels of neutral sodium. The first excited state will be the $3s$ of sodium, whose energy is given by the negative of the ionization potential, about $41,400 \text{ cm}^{-1}$. As the distance decreases, this energy level will rise on account of a Madelung term, broadening as atoms overlap, much as the $3s$ levels in a lattice of sodium atoms, so that at the normal distance of separation the band will be very broad, much broader than the occupied bands in the crystal.

Another feature complicates this situation, however. We have considered only excited states of sodium, not of chlorine. This is correct at large distance, for the chlorine problem in question is an electron in the field of a negative chlorine ion, which has no discrete stationary states. Of course, however, it has continuous energy levels, beginning at the energy zero at infinite separation. We consider how the bottom of this continuum changes with lattice spacing. At first sight, we might think the energy would decrease with a Madelung term, as with electrons bound to chlorine. This will not be the case, since the wave function connected with the continuum is distributed over space, and part of the charge is near chlorines, part near sodiums. As the distance decreases, the potential energy of the electron will decrease when it happens to be near a chlorine ion, increase when it is near sodium, compared to the value at infinite separation. The result will be to a first approximation no change in energy with distance, the opposing tendencies canceling. To a higher approximation, the decrease of potential energy near the chlorines will tend to concentrate the charge there, making its wave function resemble a discrete chlorine function more than at infinite separation, so that there will be some decrease of energy with distance, though not as much as for a pure chlorine level. Now it is evident from Fig. 1 that the re-

sulting level will cross the first excited sodium level, at about the distance of separation where the sodium level begins to split up (roughly $d=15\text{A}$). There will then be an interaction of the two types of level, the resulting lower level having a wave function with appreciable charge on both chlorine and sodium ions, behaving around a chlorine like the lowest member of the continuum, around the sodium like a $3s$ electron. The level will broaden, but will neither rise as much as a sodium level would, nor fall as much as a chlorine level. A hypothetical form for the broadened level is indicated in Fig. 1.

OPTICAL ABSORPTION FREQUENCIES

The energy levels of Fig. 1 may be used to investigate the optical absorption frequencies of the crystal. As always with one-electron energy levels, we may interpret an absorption as a transition of an electron from one of the lower, occupied levels to one of the higher, unoccupied ones, the energy difference in the diagram giving the absorption frequency. Thus we may expect an absorption in the near ultraviolet when a chlorine $3p$ electron is raised to the excited states; a shorter wave-length for chlorine $3s$; still shorter for sodium $2p$; and one in the very far ultraviolet for sodium $2s$. The near ultraviolet absorption should start at a frequency equal to the smallest interval between $3p$ and excited bands (roughly $60,000 \text{ cm}^{-1}$), with a continuum on the short wave-length side. The band is observed to start at about 1750A ($57,000 \text{ cm}^{-1}$), and to come to a sharp peak at something less than 1600A ($62,500 \text{ cm}^{-1}$). The chlorine $3s$ absorption should be expected at about $170,000 \text{ cm}^{-1}$ (590A), the sodium $2p$ at $290,000 \text{ cm}^{-1}$ (345A), and sodium $2s$ at $550,000 \text{ cm}^{-1}$ (181A). The observed absorptions resemble those predicted by the theory, but are different in detail. Thus though the near ultraviolet absorption comes at about the right place, sharp lines as well as continuous absorption are found by Hilsch and Pohl.¹ Smith finds absorption all through the region around 600A , but with pronounced peaks about 550A , 650A , and a smaller one at 900A . O'Bryan observes a fairly sharp band at 372A , rather than a broader continuum, and Smith finds a similar sharp absorption peak at about the same place. In general, more structure

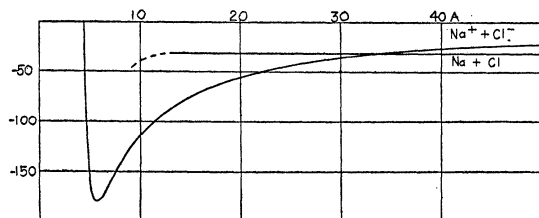


FIG. 2. Total energy of NaCl crystal, in ionic and atomic states, in kcal. per g mol.

and sharp lines are found in the absorption than the theory would suggest. We shall examine the discrepancies in the next section, showing that the method of lattice functions is only partly applicable to the problem, and that a correct solution must be obtained by considering the energy levels of the crystal as a whole. The picture of Fig. 1 remains, however, correct enough to be very suggestive. In regard to the near ultraviolet absorption, we may note an interesting approximation which we may make for the frequency of the limit. The bottom of the continuum of excited levels has risen, at the actual lattice space, about as far above the sodium $3s$ level as the top of the chlorine $3p$ is above the Madelung energy. Thus approximately the excitation energy is equal to the chlorine electron affinity, plus the Madelung energy, minus the sodium ionization potential, or numerically $30,400 + 72,000 - 41,400 = 61,000 \text{ cm}^{-1}$. This simple approximation, already suggested on somewhat different grounds by Hilsch and Pohl, gives surprisingly good results for the absorption limits of all the alkali halides.

ENERGY LEVELS OF THE CRYSTAL AS A WHOLE: NORMAL STATE

As a next step, instead of considering lattice functions and one-electron energies, we shall examine the energy levels of the crystal as a whole as a function of lattice spacing. The energy in the normal electronic state has been discussed in a well-known way by Born and others.¹² Starting at infinite separation from the state composed of sodium and chlorine ions, the energy decreases by the amount $-3.495 e^2/d$ per molecule, until a lattice spacing near the normal value is reached, when a repulsive term, often approximated by a formula a/d^n , where a is a con-

¹² See for example Wolf and Herzfeld, reference 4.

stant, n a high exponent, rather suddenly sets in, resulting in a minimum of the curve. It is to be noted that the ionic state is not the lowest energy at infinite separation. Instead, the state of neutral atoms is lower, by an amount equal to the difference between the ionization potential of sodium and the electron affinity of chlorine, per molecule. This is shown in Fig. 2, in which it is seen that the ionic and atomic states have energy levels which cross at a large value of d , about $35A$. It is closely connected with the fact that the lattice energies of Na $3s$ and $Cl^- 3p$ cross at large distances (beyond the range of Fig. 1), so that electrons from chlorine ions can be transferred to sodium ions at large distance with liberation of energy. For all our purposes, however, we may confine ourselves to distances less than this value, so that we may regard the normal state as being formed of ions.

Next, we consider excited states in which one electron is excited, the only kind which will have appreciable optical transition probabilities from the normal state. On the scale of Fig. 2, these energy levels as functions of distance will be indistinguishable from the normal state, for the energy of Fig. 2 is the energy of all N molecules of the crystal, whereas the energy of only one molecule changes on excitation, making a change in energy of the order of $1/N$ of the value of Fig. 2. To get a quantity which can be plotted, we must take the energy difference between normal and excited states, regarded as a function of lattice spacing, giving the frequency of optical absorption by the crystal. Excitation can take place in several ways: either a sodium or a chlorine electron can be excited, and it can find a resting place in an excited state of the ion in which it was originally located, or in another ion of the same or opposite sign.

SODIUM EXCITATION

Let us take up the various sorts of excitation in detail, now making use of an atomic point of view, localizing the electrons on definite ions. First, we consider the case of excitation of a sodium electron, in particular the removal of a $2p$ electron from a sodium ion, the electron going into a $3s$ state either on the same or another sodium ion. At infinite lattice spacing, the two processes, roughly equivalent to excitation and

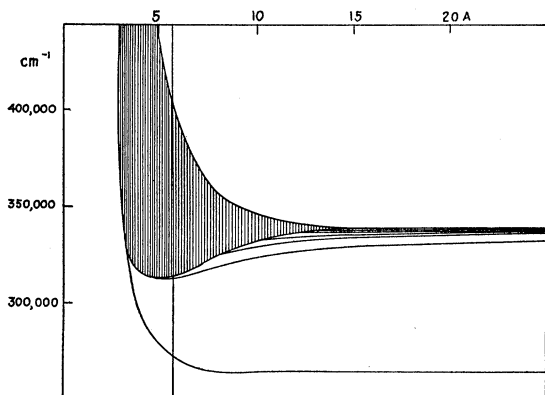


FIG. 3. Optical absorption from Na $2p$ level to lowest excited level, in NaCl.

ionization, are quite distinct. The excitation of a sodium ion to the state $2p^53s$ requires about $265,000 \text{ cm}^{-1}$, while the removal of a $2p$ electron requires about $381,000 \text{ cm}^{-1}$, of which about $41,500 \text{ cm}^{-1}$ is regained when the ionized electron attaches itself to another ion to produce a neutral atom, leaving a net energy of excitation of $339,500 \text{ cm}^{-1}$. At finite separation, however, the ionized state splits up; for if the removed electron is attached to an ion at distance D from the ion it has left, the necessary work is less than $339,500 \text{ cm}^{-1}$ by the electrostatic energy e^2/D , which would have to be expended to remove the electron the additional distance from D to infinity. Now D can have only certain definite values, for it is the distance from one sodium to another in the lattice. Thus it can have the values $(d/2)(n_1^2 + n_2^2 + n_3^2)^{1/2}$, where n_1, n_2, n_3 are three integers giving the relative positions of the two sodiums, and where the sum $n_1 + n_2 + n_3$ must be even. We thus have a discrete set of levels, approaching the value $339,500 \text{ cm}^{-1}$ as a limit. In Fig. 3 for distances greater than 15A we show some of these levels as a function of d . At large distances, the levels involving ionization cluster together, far above the level involving only excitation, but as we approach the actual lattice spacing the spread of the ionized levels is considerable.

As we approach the actual distance of separation, it no longer is possible to localize electrons on the ions, so that the method of discussion we have just used becomes inapplicable. On the other hand, the method of lattice functions,

discussed in the earlier sections, becomes increasingly appropriate. For the removal of a sodium $2p$ electron to an excited level, which we are now considering, we should take the energy difference, from Fig. 1, between the corresponding levels. Since the sodium $2p$ level is not appreciably split up at this distance, the continuum of absorption frequencies on the method of lattice functions will have the same form as the continuum of excited levels but with the Madelung function of the sodium $2p$ subtracted off. The resulting continuum is shown for small distances in Fig. 3.

We now meet the problem of correlating the two methods of approximation to the excited states, the method of atomic excitation or ionization to neighboring ions for large distances, the method of lattice functions and energy bands at small distances. Quite without calculation, we should expect that in regions where the total splitting given by the lattice model was small compared with the separations of the various ionized or excited states, the method of atomic excitation would give the correct levels, while with very wide energy bands in the lattice model, that model would give correct results. With this in mind, the various discrete levels of the atomic and ionic method have been merged into the lattice energy band of Fig. 3 at small distances, indicating a plausible construction for the excited energy levels at intermediate distances. The relations between the two methods, however, are so important that we examine them in more detail in the next section, reserving the more mathematical parts of the discussion for the Appendix.

CORRELATION OF LATTICE AND ATOMIC WAVE FUNCTIONS

In a general way, the method of lattice functions is analogous to the method of molecular orbitals, and that of atomic excitation to that of Heitler and London, in molecular problems. The inclusion of both atomic excitation and ionization corresponds to the inclusion of both nonpolar and polar states in Heitler and London's method. As one of the authors has pointed out on several occasions,¹³ the two methods are then equivalent. The wave functions formed from molecular orbi-

¹³ J. C. Slater, Phys. Rev. **35**, 509 (1930); **41**, 255 (1932).

tals can be written as linear combinations of those formed from nonpolar and polar Heitler and London functions, and *vice versa*. A correct treatment of the secular equation from either point of view will then lead to the same energy levels, though an incomplete or first order perturbation treatment will not. Let us consider first the nature of the wave functions in this problem, starting with the method of lattice functions.

The properties of single lattice functions are well known from the theory of metals.¹⁴ Each function behaves like an atomic function near each atom, but is multiplied by $\exp i(\mathbf{k}\cdot\mathbf{R})$ going from one atom to another a vector distance \mathbf{R} away, where \mathbf{k} is a vector analogous to the momentum of a plane wave. Corresponding to a single atomic wave function, there are as many lattice functions as there are atoms in the crystal, having different vectors \mathbf{k} . A filled band, then, contains one electron per atom of each spin, with the \mathbf{k} 's so arranged that there are as many positive as negative, and the vector sum of all \mathbf{k} 's is zero. This is the situation of the electrons in the normal state of an ionic lattice, where all energy bands are filled or entirely empty.

If one electron is excited, in our particular case, the band of $2p$ electrons lacks one wave function, the $3s$ band has just one occupied function. For simplicity, we neglect orbital and spin degeneracy in describing the situation. Then there are N^2 excited states, with different energies; for the electron could be removed from any one of the N $2p$ states, going into any one of the N $3s$ states. Each excited state is characterized by a value of the vector sum $\mathbf{K}=\mathbf{k}_q-\mathbf{k}_p$, where \mathbf{k}_p is the momentum of the removed $2p$ electron, \mathbf{k}_q of the $3s$, and of the N^2 states there will be N with each possible value \mathbf{K} . This quantity \mathbf{K} has great importance, on account of certain selection principles. In the first place, by optical excitation by light of wave-length λ , the transition probability is zero except to states of one particular \mathbf{K} value, equal to $2\pi/\lambda$, and pointing in the direction of the wave normal. On account of the long optical wave-lengths, this \mathbf{K} value is almost zero, so that we need consider only the excited state of $\mathbf{K}=0$. In the second place, when we use our lattice functions as the basis of a perturbation calculation,

we find that the matrix component of the perturbing energy between states of different \mathbf{K} values is always zero. Thus in all our work we can separate off the states of a particular \mathbf{K} , and treat them entirely by themselves, as if the others did not exist.

For each stationary state, we form an anti-symmetric wave function for the electrons of the whole crystal, one for the normal state, N^2 for the excited states, and set up the matrix components of energy between the various approximate wave functions. First, we consider the diagonal matrix components for the excited states. Subtracting the diagonal energy of the normal state from that of the excited state, to get the excitation energy, we find just the difference between the one-electron energies of the $3s$ and $2p$ electrons of appropriate \mathbf{k} values, in the lattice energy bands, as indicated by the shaded band of Fig. 3. At infinite separation this band shrinks to the single level corresponding to ionization of one sodium ion, attachment of the electron to another ion at infinite distance. For with the lattice functions, each electron is uniformly distributed over all the atoms. The removed $2p$ electron, and the $3s$, are equally and independently likely to be found on any one of the N atoms, so that the chance that they are on neighboring atoms, decreasing the energy appreciably on that account, is negligible. As far as diagonal energy is concerned, in other words, the method of lattice functions takes no account of the possibility of excitation, or of ionization and removal to nearby atoms.

It must not be supposed, however, that because individual lattice states are poor approximations to the actual states at large distances, they cannot be used as a starting point for a perturbation calculation. Instead, we can find the nondiagonal terms of the energy, which not only are different from zero between states of the same \mathbf{K} value, but remain important at large lattice spaces. It is easy at large distances to solve the perturbation problem exactly, and to find the correct linear combinations of lattice functions, which may be easily described. In the first place, we may take all the lattice functions, with all their N^2 combinations of values of \mathbf{k}_p and \mathbf{k}_q , multiply each one by the simple coefficient $(1/N) \exp i(\mathbf{k}_p\cdot\mathbf{R}_m-\mathbf{k}_q\cdot\mathbf{R}_n)$, where \mathbf{R}_m and \mathbf{R}_n

¹⁴ For instance, J. C. Slater, Rev. Mod. Phys. 6, 209 (1934).

are the vector positions of two particular sodium atoms in the lattice, and add. The result is similar to the well-known process of building up a wave packet out of plane waves, forming a localized disturbance. It gives a wave function in which there is one electron on each atom except that with position \mathbf{R}_m , which has no electron, and that at \mathbf{R}_n , which has an extra electron, in a $3s$ state. In other words, its wave function is precisely the atomic function which we have discussed previously. When we compute the diagonal energy of such a wave function, we find that it is just the value plotted in Fig. 3 at large distances. In particular, for $\mathbf{R}_m = \mathbf{R}_n$, a $2p$ electron is merely excited to a $3s$ state in the same atom. The non-diagonal energy component between two such atomic states at large distances is zero, so that these states form the correct solution of the problem.

The atomic functions, with a $2p$ electron missing from the atom at \mathbf{R}_m , and present as a $3s$ on that at \mathbf{R}_n , are correct solutions at large distance, but they are degenerate. The energy depends only on the vector distance $\mathbf{R}_m - \mathbf{R}_n$ (whose magnitude was previously called D), not on \mathbf{R}_m and \mathbf{R}_n separately. In other words, any atom of the crystal may be excited or ionized, so that there are N states of the same energy, corresponding to each value of $\mathbf{R}_m - \mathbf{R}_n$. Any linear combinations of these N states of the same energy would be legitimate functions at large distances, but one particular set of combinations has the property of being appropriate for smaller distances as well, that set in which each function is characterized by a particular value of the same vector \mathbf{K} which we have mentioned above. Such a function represents a sort of wave of excitation or ionization, traveling along with a wave number \mathbf{K} . These waves of excitation have been described by Frenkel, though without making this connection with the lattice functions, and without discussing the waves of ionization (the case $\mathbf{R}_m - \mathbf{R}_n \neq 0$). For most purposes there is no great advantage in using them, and we may use the atomic functions instead.

If we could now solve our perturbation problem for intermediate distances, as we can for large distances, we should find exactly how the levels at large and small distances were connected. This unfortunately cannot be done. As

the atoms begin to overlap, nondiagonal matrix components of energy appear between two atomic states, or two excitation wave states, in which the excited electrons are situated on neighboring atoms. By a second-order perturbation calculation we can see that, as the continuum of lattice energy levels begins to broaden out, the excitation state will be somewhat depressed by the action of neighboring states, while the ionized states will be pushed almost equally from above and below, and will be practically unaffected until the lattice energy band is decidedly broad. As we approach the observed distance, however, this perturbation calculation becomes inaccurate. Using an approximate model, it has been possible to follow the behavior of the excitation state, and to show that this gradually merges into the bottom of the continuum, though at the actual lattice spacing it will still be distinct. The ionization states will also merge into the continuum, at larger distances, though it has been impossible to work this out in detail. At any distance, most of the levels will form practically a continuum, with a few discrete levels at the bottom, the number of discrete levels decreasing as the lattice spacing decreases. The levels in Fig. 3 have been drawn for intermediate distances according to these principles, the position of the lowest, excitation level being given approximately by our calculation.

Before considering the agreement with experiment, we must examine not only the position of the excited levels, but also the transition probabilities to them. At large distances, we can see without calculation that the probability of transition to an ionized state is zero, the only transitions being to the excited state. For the transition probability involves the matrix component of electric current between the normal and excited states, the wave functions of these states do not overlap if they correspond to having electrons on different atoms, and the matrix component and transition probability are correspondingly zero. Thus the lowest level takes all the transition probability at large distances. At small distances where the lattice functions are correct, on the other hand, the matrix components are of the same order of magnitude for all the possible transitions in the band. By making the proper transformation, we can calculate the matrix com-

ponents corresponding to the excitation and ionization waves at large distances, in terms of the lattice components. We find, as we should expect, that the particular combination of lattice functions corresponding to the excitation wave then acquires the whole transition probability, the other combinations losing their probabilities. But now at the actual distance of separation, neither the excitation and ionization waves, nor the lattice functions, form the correct wave functions, but combinations of them, so that the transition probabilities will be intermediate between these limiting cases. From Fig. 3, we see that the excitation wave will still be far removed from the continuum at the actual distance, so that we may expect that it will still have the larger part of the transition probability; but it will have lost part of its intensity to the continuum, which will have a total intensity to make up for the intensity lost by the discrete line. It is possible that the next line, corresponding to ionization and attachment of the electron to the nearest neighbor, may still be slightly separated from the continuum, and that it may have an appreciable intensity, since at small distances the wave function of an excited atom may appreciably overlap that of the nearest neighbor. Thus there will be one, perhaps two, discrete lines, then a continuum, and the relative intensities cannot be well estimated.

From Fig. 3, we should then expect a sharp line absorption in NaCl corresponding to 271,000 cm^{-1} (369Å), perhaps another sharp line at about 312,000 (320Å), and a continuum beginning at just about that point, toward the ultraviolet. O'Bryan³ observes an absorption band at 372Å, but has not observed further bands, perhaps because they have not enough intensity. For the lithium salts, however, he observes more detail. The corresponding sharp line transitions in lithium should be at about 476,000 cm^{-1} (210Å). O'Bryan observes in LiCl a sharp line at 204Å (490,000 cm^{-1}), another at 192Å (520,000 cm^{-1}), and continuous absorption beyond that, as we should expect. For the potassium crystals, one should expect an absorption at about 165,000 cm^{-1} (605Å), and Smith observes absorption at about 540Å in KCl, 510Å in KI, which may be the corresponding bands. Both the observations and the theory thus seem to agree in demanding

excitation waves for the lowest excited states, merging then into something much like the lattice states forming a continuum, though further experimental evidence would be very desirable.

We have been considering the transition from the sodium $2p$ state to the first excited state, which is largely like sodium $3s$, but has some of the properties of an excited chlorine state. The discussion of transitions from other sodium states, as $2s$, would proceed in a very similar way, with similar structure in the absorption band, further in the ultraviolet, as is seen most easily from Fig. 2. In connection with the excited states, we have spoken only of the lowest band, but should remember that the sodium $3p$, $3d$, $4s$ -levels at large distances will all split into lattice bands at smaller distances, becoming mixed up with chlorine bands, and resulting in a continuum of great complexity. This continuum will have concentrations of density at some energies, deficiencies at others, and the resulting continuous absorption will show maxima and minima which may be striking, and which may give the effect of further sharp lines. Taken in connection with the sharp line structure already described, we see that the absorption spectrum can have a very complicated appearance, one very difficult to work out in detail.

CHLORINE EXCITATION

Next, we consider the near ultraviolet absorption, in which a chlorine $3p$ electron is excited to the same lattice level as before. The excited level at large distances would correspond to the removal of an electron from the chlorine, and its attachment to a sodium, and would have no probability of occurrence on account of non-overlapping wave functions. At small distances, however, we have seen that the excited level acquires some of the properties of an excited chlorine state, and has a large probability of transition from the normal state. We can now proceed as before to find the excited levels at large and small distances. At large distances, the required energy is the electron affinity of chlorine, minus the ionization potential of sodium, plus a Madelung term. This term is different from what it was before, for the potential energy of an electron near a sodium ion is greater than that near

a chlorine by $2(3.495)e^2/d$, so that this term appears in the Madelung energy. In addition, if the sodium is only a distance D from the a chlorine, there is the same negative contribution $-e^2/D$ as before, so that the total excitation energy is (electron affinity) - (ionization potential) $+2(3.495)e^2/d - e^2/D$. As before, D can have an infinite number of values, depending on how far the electron is removed from the chlorine, but now the set of D values will be different from before, starting with the distance from a chlorine to its nearest sodium neighbor ($d/2$), and so on. The resulting sharp levels at large distance are drawn in Fig. 4. The levels become negative at large distances, as can also be seen from Fig. 1, and as would be expected from Fig. 2, from the fact that the atomic state rather than the ionic is the stable one at large distances, and that the process now being contemplated is one in which a chlorine and sodium ion exchange electrons to become neutralized.

At the actual lattice spacing, von Hippel⁶ has essentially used the discrete levels we have just described, and has tried to correlate them with the observed structure in the absorption band. It is hardly possible that this is correct, for at these smaller distances the lattice method becomes reasonable, and entirely changes the situation. In Fig. 4 we have drawn the absorption continuum to be expected from the lattice method, remembering that the broadening now comes both from the normal, chlorine $3p$ lattice state and the excited state. For a given \mathbf{K} value this

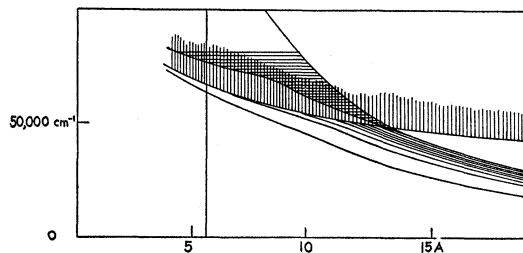


FIG. 4. Optical absorption from Cl $3p$ level to lowest excited level, in NaCl.

becomes a perfectly definite band, with N excited levels, as before. It is now easy to draw the interpolated levels, much as we have done in Fig. 3. In this case, there is nothing like the excited state in the sodium-sodium transition, simply a continuous absorption edge at large distances, lying well above the discrete levels, and merging with the continuum we have drawn at smaller distances. As far as agreement with experiment is concerned, we have already seen that the absorption edge comes at about the right place, and it is plain that it should be expected to show structure. The observations of Hilsch and Pohl on sodium chloride do not extend far enough into the ultraviolet to show much of this structure, though for some of the alkali halides a great deal is observed. It appears at any rate that the present type of theory, involving both sharp line and continuous absorption, is the correct sort to explain the details, but more elaborate calculation is probably necessary to work them out in specific cases.

APPENDIX

Consider a lattice of N atoms, each normally having one electron, all of the same spin. Assume the wave function of an electron about one of the nuclei, in the absence of the other nuclei, is $u(\mathbf{r}-\mathbf{R})$ for the normal state, $v(\mathbf{r}-\mathbf{R})$ for the only excited state we shall consider, where \mathbf{r} is the coordinate of the electron, \mathbf{R} of the nucleus. These functions are assumed to be normalized to unity. Then Bloch's approximation to a modulated one-electron function for the normal state is $(1/(N)^{1/2}) \sum_s \exp(i(\mathbf{k} \cdot \mathbf{R}_s)) u(\mathbf{r}-\mathbf{R}_s)$, where \mathbf{k} is a momentum-like vector. The factor $1/(N)^{1/2}$ takes care of normalization if the wave functions u of different atoms do not overlap, but there are small corrections, which we shall neglect, on account of normalization at smaller distances. There are N values $\mathbf{k}_1 \cdots \mathbf{k}_N$ corresponding to the N Bloch functions in a completed band. Similar Bloch functions can be set up for an excited electron, using v instead of u . Next we can set up anti-

symmetric functions of the electron coordinates, to represent the state of the whole crystal. If we have the normal state, with no excited electrons, the antisymmetric function, which we may call $B(0)$, is the determinant

$$B(0) = (1/(N)!) \left| (1/(N)^{1/2}) \sum_s \exp(i(\mathbf{k}_j \cdot \mathbf{R}_s)) u(\mathbf{r}_\sigma - \mathbf{R}_s) \right|,$$

the elements of the determinant corresponding to all N values of f and g . This state is likewise approximately normalized. For an excited state with one electron excited, we may imagine that the one-electron function with \mathbf{k}_p is missing, and is replaced by a one-electron function formed from the excited function v , with momentum \mathbf{k}_q . This function, which we call $B(p, q)$, is the determinant formed just like $B(0)$, but with terms

$$(1/(N)^{1/2}) \sum_s \exp(i(\mathbf{k}_q \cdot \mathbf{R}_s)) v(\mathbf{r}_\sigma - \mathbf{R}_s)$$

in place of

$$(1/(N)^{1/2}) \sum_s \exp(i(\mathbf{k}_p \cdot \mathbf{R}_s)) u(\mathbf{r}_\sigma - \mathbf{R}_s)$$

in the p th row. There will be N^2 states $B(p, q)$, since either of the indices p, q can take on any one of N values.

Next, consider functions built up in the atomic way from the u 's and v 's. The normal state corresponds to having one electron in state u about each nucleus, and its antisymmetric wave function, which we may call $A(0)$, is

$$A(0) = (1/(N!)^{1/2}) |u(\mathbf{r}_f - \mathbf{R}_g)|,$$

which again is normalized at large lattice spacings. By making suitable combinations of rows in the determinant, it is easily shown that $A(0) = B(0)$, so that the normal state is identical in the atomic or the lattice method. The excited states in the atomic method are set up by assuming the electron to be removed from the m th atom, and to be present in an excited state in the n th atom. The corresponding function $A(m, n)$ is a determinant like the preceding one, but with the terms $u(\mathbf{r}_f - \mathbf{R}_m)$ missing, and replaced by $v(\mathbf{r}_f - \mathbf{R}_n)$. In particular, if $m = n$, the state is one with the m th atom excited, while if $m \neq n$, the m th atom is positively ionized, the n th negatively. Again there are N^2 excited states, corresponding to all N values of m and n separately.

Each term in the expansion of the function $A(m, n)$ is a product of $(N-1)$ factors u , and one factor v ; one of the nuclei, the m th, has no electron, and another, the n th, has two, one in state u and the other v . Similarly each term in the expansion of $B(p, q)$ is a product of $(N-1)$ factors u , and one factor v . It is not obvious that in the expansion the only terms are those with all nuclei but two occupied by one electron each, one of the remaining ones with two, and the final one with none, but this is actually the case on account of the antisymmetry, and the resulting application of the exclusion principle: no two functions u can be found on the same nucleus, so that the only possible doubling up of electrons on atoms is the single case of a function v and a function u on the same atom. The complete set of functions $A(m, n)$ thus involve the same terms as the set $B(p, q)$, and since each set is normalized and orthogonal at large distances of separation, it is obvious that one set can be derived from the other by a unitary transformation. Thus we must have $A(m, n) = \sum_{p, q} C(m, n; p, q) B(p, q)$. To find the coefficients C , we may multiply by $B^*(p', q')$ and integrate over the electron coordinates. Then by the normalization and orthogonality of the B 's,

$$C(m, n; p, q) = \int A(m, n) B^*(p, q) d\tau.$$

We must now find the integral above, which is the integral of a product of two determinants. Consider the integral of a typical term of the determinant A , multiplied by the diagonal term of B^* . This is

$$\begin{aligned} & 1/(N!(N^N)^{1/2}) \int \dots \int u(\mathbf{r}_a - \mathbf{R}_1) u(\mathbf{r}_b - \mathbf{R}_2) \\ & \quad \cdot u(\mathbf{r}_i - \mathbf{R}_{m-1}) v(\mathbf{r}_j - \mathbf{R}_n) u(\mathbf{r}_k - \mathbf{R}_{m+1}) \\ & \quad \cdot u(\mathbf{r}_z - \mathbf{R}_N) \left\{ \sum_{s_1} \exp -i(\mathbf{k}_1 \cdot \mathbf{R}_{s_1}) u(\mathbf{r}_1 - \mathbf{R}_{s_1}) \right\} \dots \\ & \left\{ \sum_{s_{p-1}} \exp -i(\mathbf{k}_{p-1} \cdot \mathbf{R}_{s_{p-1}}) u(\mathbf{r}_{p-1} - \mathbf{R}_{s_{p-1}}) \right\} \\ & \left\{ \sum_{s_p} \exp -i(\mathbf{k}_q \cdot \mathbf{R}_{s_p}) v(\mathbf{r}_p - \mathbf{R}_{s_p}) \right\} \\ & \left\{ \sum_{s_{p+1}} \exp -i(\mathbf{k}_{p+1} \cdot \mathbf{R}_{s_{p+1}}) u(\mathbf{r}_{p+1} - \mathbf{R}_{s_{p+1}}) \right\} \dots \\ & \left\{ \sum_{s_N} \exp -i(\mathbf{k}_N \cdot \mathbf{R}_N) u(\mathbf{r}_N - \mathbf{R}_N) \right\} d\tau_1 \dots d\tau_N, \end{aligned}$$

where $ab \dots ijk \dots z$ form a typical permutation of the indices $1 2 \dots N$. The integral over the a th electron has as an integrand $u(\mathbf{r}_a - \mathbf{R}_1) \sum_s \exp -i(\mathbf{k}_a \cdot \mathbf{R}_s) u(\mathbf{r}_a - \mathbf{R}_s)$ (unless a

happens to equal p). If we neglect the lack of orthogonality of u 's belonging to different atoms, the only term of this summation giving an integral different from zero is that for $s=1$, which integrates to $\exp -i(\mathbf{k}_a \cdot \mathbf{R}_1)$. With certain exceptions, the terms all integrate in similar ways, giving $\exp -i(\mathbf{k}_b \cdot \mathbf{R}_2), \dots \exp -i(\mathbf{k}_z \cdot \mathbf{R}_N)$. The exceptional terms are the following: If $a=p$, on account of the orthogonality of the u 's and v 's, the integral over the a th electron gives zero, and the whole integral vanishes. The same thing holds if b, c , or any of the indices except j , is equal to p . Thus the only terms of the product which do not integrate to zero are those with $j=p$. If $j=p$, so that the integral does not vanish, then for the j th electron we must integrate $v(\mathbf{r}_j - \mathbf{R}_n) \sum_s \exp -i(\mathbf{k}_q \cdot \mathbf{R}_{s_p}) v(\mathbf{r}_p - \mathbf{R}_{s_p})$. The only term different from zero is for $s_p=n$, giving $\exp -i(\mathbf{k}_q \cdot \mathbf{R}_n)$.

When we take all terms corresponding to all permutations $a \dots z$, we see that except for the exceptional terms mentioned just above, the result could be written as a determinant, $(1/N!) |\exp -i(\mathbf{k}_f \cdot \mathbf{R}_g)/(N)^{1/2}|$, where f and g take on all values. The same result is obtained on multiplying the determinant $A(m, n)$ with each of the $N!$ terms of the determinant $B^*(p, q)$, so that the result is just $N!$ times as great, cancelling the factor $N!$ in the denominator. This determinant is just the determinant of the coefficients of expansion from the atomic functions $u(\mathbf{r} - \mathbf{R}_g)$ to the Bloch one-electron functions $(1/(N)^{1/2}) \sum_s \exp i(\mathbf{k}_f \cdot \mathbf{R}_s) u(\mathbf{r} - \mathbf{R}_s)$, and

since both sets of functions to our approximation are normalized and orthogonal, the transformation from one set of functions to the other is a unitary transformation, so that the determinant of coefficients is of unit magnitude, and may be set equal to $\exp i\theta$. This shows immediately that $|\int A(0) B^*(0) d\tau| = 1$, as it should. But now on account of our exceptional terms, the integral has a different value in our case. It is easily seen that it is now the determinant of terms $(\exp -i(\mathbf{k}_f \cdot \mathbf{R}_g))/(N)^{1/2}$, in which all terms of the row $f=p$, and of the column $g=m$, are set equal to zero, except the term $f=p, g=m$, which equals $(\exp -i(\mathbf{k}_q \cdot \mathbf{R}_n))/(N)^{1/2}$. The result is then equal to $(\exp -i(\mathbf{k}_q \cdot \mathbf{R}_n))/(N)^{1/2}$ times the minor of the determinant $|\exp -i(\mathbf{k}_f \cdot \mathbf{R}_g)/(N)^{1/2}|$ corresponding to $f=p, g=m$. But the minor corresponding to a certain term in the determinant of coefficients of a unitary transformation equals the complex conjugate of the term itself, multiplied by the value of the determinant, so that finally the coefficient in question is given by

$$C(m, n; p, q) = (1/N) \exp i(\mathbf{k}_p \cdot \mathbf{R}_m - \mathbf{k}_q \cdot \mathbf{R}_n) \exp i\theta.$$

The factor $\exp i\theta$ is a phase factor which we shall henceforth neglect, since it is the same for all functions.

We now see that we can write an atomic function as

$$A(m, n) = 1/N \sum_{p, q} \exp i(\mathbf{k}_p \cdot \mathbf{R}_m - \mathbf{k}_q \cdot \mathbf{R}_n) B(p, q).$$

We can rearrange the double summation, so as to sum first over all values of p and q for which $\mathbf{k}_q - \mathbf{k}_p = \mathbf{K}$ is constant. Thus

$$A(m, n) = \sum_{\mathbf{K}} \frac{\exp -i(\mathbf{K} \cdot \mathbf{R}_n)}{(N)^{1/2}} \sum_{\mathbf{k}} \frac{\exp i(\mathbf{k} \cdot \mathbf{R}_m)}{(N)^{1/2}} B(\mathbf{k} - \mathbf{K}, \mathbf{k}),$$

where we have used the relation

$$\mathbf{k}_p \cdot \mathbf{R}_m - \mathbf{k}_q \cdot \mathbf{R}_n = -(\mathbf{k}_q - \mathbf{k}_p) \cdot \mathbf{R}_n + \mathbf{k}_q \cdot (\mathbf{R}_m - \mathbf{R}_n) = -\mathbf{K} \cdot \mathbf{R}_n + \mathbf{k} \cdot \mathbf{R},$$

setting $\mathbf{k}_q \equiv \mathbf{k}$, $\mathbf{R}_m - \mathbf{R}_n = \mathbf{R}$.

Now we can form the function

$$E(\mathbf{K}, \mathbf{R}) = \sum_{\substack{\mathbf{R}_n \\ \mathbf{R}_n = \text{const.}}} \frac{\exp i(\mathbf{K} \cdot \mathbf{R}_n)}{(N)^{\frac{1}{2}}} A(m, n),$$

an excitation or ionization wave of momentum vector \mathbf{K} , corresponding to an electron in each atom being removed to the atom distant by the vector displacement \mathbf{R} . This is given by

$$E(\mathbf{K}, \mathbf{R}) = \sum_{\mathbf{K}', \mathbf{k}} \frac{\exp i(\mathbf{k} \cdot \mathbf{R})}{(N)^{\frac{1}{2}}} B(\mathbf{k} - \mathbf{K}', \mathbf{k}) \sum_{\mathbf{R}_n} \frac{\exp i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{R}_n}{N}$$

But by the properties of the reciprocal lattice,

$$\sum_{\mathbf{R}_n} \exp i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{R}_n = 0 \text{ if } \mathbf{K} - \mathbf{K}' \neq 0, = N \text{ if } \mathbf{K} - \mathbf{K}' = 0.$$

Thus $E(\mathbf{K}, \mathbf{R}) = \sum_{\mathbf{k}} \frac{\exp i(\mathbf{k} \cdot \mathbf{R})}{(N)^{\frac{1}{2}}} B(\mathbf{k} - \mathbf{K}, \mathbf{k})$,

so that, as stated in the text, this excitation function is equal, except for the factor $(\exp -i(\mathbf{K} \cdot \mathbf{R}_n))/(N)^{\frac{1}{2}}$, to the same summation over Bloch functions which we should carry out to get an atomic function, with the exception that the summation is to be carried out only for terms of a given \mathbf{K} value.

Now that we have exhibited the transformation coefficients between the Bloch functions B , the atomic functions A , and the excitation wave functions E , we shall find matrix components of the energy. We shall do this for the atomic functions, using the transformation theory to get matrix components between the other types of functions. We must make more precise assumptions than previously about the energy. We assume that the N electrons move in a potential field $U(\mathbf{r})$, which can be written as a sum of potentials from each nucleus: $U(\mathbf{r}) = \sum_s V(\mathbf{r} - \mathbf{R}_s)$, in which \mathbf{R}_s is the vector coordinate of the s th nucleus, and $V(\mathbf{r})$ is the potential of a singly charged positive ion, reducing to $-2/r$ in atomic units, at large values of r , but behaving differently for small r , as the nucleus is no longer well shielded by the electrons of the core. Since our problem is that of N electrons moving in this field, it is plain that the electrons will on the average cancel this nuclear charge, so that an electron at a given point of the lattice will be acted on only by its near neighbors. Then, in atomic units the energy operator is

$$H = -\sum_i \nabla_i^2 + \sum_{\substack{\text{pairs} \\ i, j}} \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i U(\mathbf{r}_i) + \sum_{\substack{\text{pairs} \\ s, t}} \frac{2}{|\mathbf{R}_s - \mathbf{R}_t|},$$

where the first term is the kinetic energy, the second the mutual potential energy of the electrons, the third the potential energy of the electrons in the fields of the cores of the atoms, and the last the mutual energy of the positive ions. Now we allow H to operate on one of the terms in the expansion of the determinant forming an atomic function $A(m, n)$. We assume that the individual factors satisfy equations

$$\begin{aligned} (-\nabla^2 + V(\mathbf{r} - \mathbf{R}_s))u(\mathbf{r} - \mathbf{R}_s) &= Eu(\mathbf{r} - \mathbf{R}_s), \\ (-\nabla^2 + V(\mathbf{r} - \mathbf{R}_s))v(\mathbf{r} - \mathbf{R}_s) &= E'v(\mathbf{r} - \mathbf{R}_s). \end{aligned}$$

Then we have

$$\begin{aligned} Hu(\mathbf{r}_1 - \mathbf{R}_1) \cdots u(\mathbf{r}_{m-1} - \mathbf{R}_{m-1})v(\mathbf{r}_m - \mathbf{R}_m)u(\mathbf{r}_{m+1} - \mathbf{R}_{m+1}) \\ \cdots u(\mathbf{r}_N - \mathbf{R}_N) = \{((N-1)E + E') + \sum_{\substack{\text{pairs} \\ i, j}} \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ + \sum_{i \neq j} (U(\mathbf{r}_i) - V(\mathbf{r}_i - \mathbf{R}_i)) + (U(\mathbf{r}_m) - V(\mathbf{r}_m - \mathbf{R}_m)) \\ + \sum_{\substack{\text{pairs} \\ s, t}} \frac{2}{|\mathbf{R}_s - \mathbf{R}_t|}\} u(\mathbf{r}_1 - \mathbf{R}_1) \cdots u(\mathbf{r}_N - \mathbf{R}_N). \end{aligned}$$

First we shall find the diagonal component of the energy matrix. As a first step, we multiply $Hu(\mathbf{r}_1 - \mathbf{R}_1) \cdots$ by the same combination of u 's and v 's already written, and integrate over the electron coordinates. In doing this, the repulsive potential terms between pairs of electrons and pairs of nuclei in general cancel the attractive terms between nuclei and electrons, so that except for a few special terms the result is simply $(N-1)E + E'$. The special terms arise because the m th electron is on the n th nucleus instead of the m th. The interaction terms between the m th electron and other electrons then integrate, if the distributions of charge are spherically symmetrical and nonoverlapping, to

$$\sum_{s \neq m, n} \frac{2}{|\mathbf{R}_n - \mathbf{R}_s|} + \int \int \frac{2}{|\mathbf{r}_m - \mathbf{r}_n|} v^*(\mathbf{r}_m - \mathbf{R}_m)v(\mathbf{r}_m - \mathbf{R}_m) \times u^*(\mathbf{r}_n - \mathbf{R}_n)u(\mathbf{r}_n - \mathbf{R}_n) d\tau_n d\tau_m,$$

where the last term represents the interaction between the normal and excited electrons on the n th nucleus, instead of

to $\sum_{s \neq m} \frac{2}{|\mathbf{R}_m - \mathbf{R}_s|}$ as we should otherwise have had. But the interaction terms between the m th electron and the nuclei become $\sum_{s \neq n} \frac{-2}{|\mathbf{R}_n - \mathbf{R}_s|}$, where we use the value of V appropriate at large distances, so that the net result is $-\frac{2}{|\mathbf{R}_m - \mathbf{R}_n|}$

+ the integral written above. Next, we multiply $Hu(\mathbf{r}_1 - \mathbf{R}_1) \cdots$ by any other terms which do not integrate to zero. We shall assume that the distance of separation of atoms is great enough so that the unexcited wave functions u do not overlap at all (as for instance the $2p$ in sodium), while the excited functions v overlap only between nearest neighbors. Then the only other function by which we may integrate to get a nonvanishing integral is that in which the two electrons on the n th atom are interchanged, and this gives an integral similar to that above, but with interchange of electrons. The net result is then, in an obvious notation,

$$\begin{aligned} (mn/H/mn) &= (N-1)E + E' + \int \int \frac{2}{|\mathbf{r}_m - \mathbf{r}_n|} \\ &\times v^*(\mathbf{r}_m - \mathbf{R}_m)v(\mathbf{r}_m - \mathbf{R}_m)u^*(\mathbf{r}_n - \mathbf{R}_n)u(\mathbf{r}_n - \mathbf{R}_n) d\tau_n d\tau_m \\ &+ \int \int \frac{2}{|\mathbf{r}_m - \mathbf{r}_n|} v^*(\mathbf{r}_n - \mathbf{R}_n)v(\mathbf{r}_m - \mathbf{R}_m)u^*(\mathbf{r}_m - \mathbf{R}_m) \\ &\times u(\mathbf{r}_n - \mathbf{R}_n) d\tau_n d\tau_m - \frac{2}{|\mathbf{R}_m - \mathbf{R}_n|}. \end{aligned}$$

If we refer to the normal state as the zero of energy, we see that $E = 0$, so that the energy of excitation is $E' - E$ plus the integrals and the Coulomb term. Now the integrals are just

the Coulomb and exchange interaction between the two electrons on the negative n th ion, so that they, taken together with $E' - E$, give the best approximation we can make with these wave functions to the energy of the negative ion, referred to the normal state of the neutral atom as zero. If we let this be ϵ_1 , we have

$$(mn/H/mn) = \epsilon_1 - \frac{2}{|\mathbf{R}_m - \mathbf{R}_n|},$$

as stated in the text. The situation is quite different, however, in the special case $m = n$, where the electron is only excited, and not removed to another atom. Here all the Coulomb terms cancel, and there is no exchange integral, since no atom has more than one electron. We then have

$$(mn/H/mn) = (N-1)E + E' = \epsilon_0,$$

where ϵ_0 is the energy required to excite a single atom without ionization, a decidedly smaller value than ϵ_1 .

We are now ready to find nondiagonal terms of the energy matrix. With the assumptions we have made, the only nonvanishing terms are those in which the excited electron only changes from one state to the other, and changes only from its position on the n th atom to one of the next neighbors n' . The only contribution comes from multiplying $Hu(\mathbf{r}_1 - \mathbf{R}_1) \cdots$, as before, with the identical function except for the exchange of $v(\mathbf{r}_m - \mathbf{R}_n)$ in place of $v(\mathbf{r}_m - \mathbf{R}_n)$. We make the crude approximation that the orthogonality integral $\int v^*(\mathbf{r}_m - \mathbf{R}_n)v(\mathbf{r}_m - \mathbf{R}_{n'})d\tau$ can be neglected. (It is somewhat more complicated, but not difficult, to carry through the calculations without making this assumption; no essential change in the conclusions is brought about thereby.) Then we have

$$(mn/H/mn') = \int \{ U(\mathbf{r}_m) - V(\mathbf{r}_m - \mathbf{R}_n) + \sum_{j \neq m} \int \frac{2}{|\mathbf{r}_m - \mathbf{r}_j|} u^*(\mathbf{r}_j - \mathbf{R}_j)u(\mathbf{r}_j - \mathbf{R}_j)d\tau_j \} v^*(\mathbf{r}_m - \mathbf{R}_{n'})v(\mathbf{r}_m - \mathbf{R}_n)d\tau_n.$$

Now $U(\mathbf{r}_m)$ plus the summation represents the potential of an electron in the field of the nuclei and of one electron per atom on every atom but the m th; that is, it is the potential in which we may assume the m th electron to be moving. The integral is then the sort met in Bloch's theory, and we may let

$$(mn/H/mn') = \beta(m, n, n').$$

So long as the n th atom is not very near the m th, the quantity β will really not depend on m , n , or n' , but will be a constant. The nondiagonal term β becomes large only when the atoms overlap each other. Thus, at large distances the energy is diagonal with respect to the atomic functions, so that they form a solution of the problem, which becomes less and less accurate as the overlapping becomes greater.

By the transformation theory we can at once find the matrix components of the energy with respect to the other types of wave functions. Using the excitation waves, we find that there is no component of energy between waves of different K value; but that with the same K value, the diagonal energy, between states with the same value of $\mathbf{R} = \mathbf{R}_m - \mathbf{R}_n$, is the same as the energy of the atomic state with the same m and n values; while the nondiagonal

energy between two states having the same m , but with n and n' in the two states, where \mathbf{R}_n and $\mathbf{R}_{n'}$ represent neighbors, is $\exp i(\mathbf{K} \cdot (\mathbf{R}_{n'} - \mathbf{R}_n))\beta(m, n, n')$. Using Bloch waves, the diagonal energy is

$$\left\{ (1 - 1/N)\epsilon_1 + (1/N)\epsilon_0 - 1/N \sum_m \frac{2}{|\mathbf{R}_0 - \mathbf{R}_m|} \right\} + \sum_{\text{nearest neighbors}} \exp -i(\mathbf{k}_q \cdot (\mathbf{R}_n - \mathbf{R}_{n'}))\bar{\beta}.$$

Here the first bracket represents the center of gravity of the band of lattice energy levels, and the second term gives the spreading, according to the usual Bloch formula. The center of gravity arises because there is one chance out of N that an electron may be just excited (energy ϵ_0), and $N-1$ chances out of N that it is ionized (energy ϵ_1), with an average electrostatic term between ions given by the summation. In the term giving the spreading, the quantity $\bar{\beta}$ is the average of β over all values of m , for a fixed n and n' . The nondiagonal energy with the Bloch functions is

$$1/N(\epsilon_0 - \epsilon_1) + 1/N \sum_m \exp i(\mathbf{k}_q - \mathbf{k}_{q'}) \cdot (\mathbf{R}_m - \mathbf{R}_0) \left\{ \frac{2}{|\mathbf{R}_m - \mathbf{R}_0|} + \sum_{n'} \exp i\mathbf{k}_{q'} \cdot (\mathbf{R}_0 - \mathbf{R}_{n'})\beta(m, 0, n') \right\}$$

if $\mathbf{k}_q - \mathbf{k}_{q'} = \mathbf{k}_p - \mathbf{k}_{p'} = 0$ otherwise. Here the first term is independent of distance, so that it becomes very important at large distances, where the energy band becomes narrow. It is the nondiagonal term responsible for splitting off the excited from the ionized states at large distances, and the summations, which fall off inversely with the lattice spacing, are responsible for the splitting up of the various ionized states.

Since there are nondiagonal components of the energy in each system of functions we have examined, no one of these sets forms a solution of Schrödinger's equation. We must instead form linear combinations, which will reduce to atomic or excitation functions at large lattice spacing, and will approach the lattice functions at small distances, without however quite reaching them until the energy band becomes of infinite width. The perturbation problem is too difficult to solve exactly, and we shall adopt approximate and schematic methods. For considerable distances of separation we can use second order perturbation theory, starting with atomic or excitation functions. Each level will be repelled by those levels obtained from it by letting its excited atom be displaced to one of its nearest neighbors, a small number of levels. The repulsion from one of these levels will be β^2 divided by the energy difference between the original level and that resulting from the displaced atom. In the first place, the whole effect is proportional to the square of β , or the square of the breadth of the lattice energy band, so that it is small. Further, for the ionized as opposed to the excited bands, opposite displacements of the electron will make opposite changes in the unperturbed energy, so that the various terms in the second order change in the energy will tend to cancel. Ionized bands, then, will have the values given by the atomic functions even when the energy bands are appreciably split up. The excited level, however, will be depressed, since all other states with which it interacts lie higher than it does.

Actually, however, we are interested in distances of separation too small for this second order perturbation to be satisfactory. It is not practicable to apply conventional perturbation theory to the Bloch functions, for they form a continuum, and the nondiagonal energy is larger than the energy differences between unperturbed functions. We shall try to investigate the behavior of the excited atomic level in this region, however, by adopting a simplified model. We take a one-dimensional lattice, so that each atom has only two nearest neighbors. Furthermore, we neglect the electrostatic interaction terms, so that we cannot expect to get correct information regarding the ionized levels. Starting with atomic functions, then, we assume the diagonal energy to be ϵ_1 for ionized states, ϵ_0 for the excited state, and we assume the nondiagonal energy to be β (a constant) between two states differing by a displacement of the excited electron to one of its two nearest neighbors. With this simplified model, we can solve the perturbation problem exactly, in the following manner.

Consider a linear crystal having N atoms, and repeated periodically, so that wave functions must satisfy periodic boundary conditions. Then there are N^2 excited states. It is most convenient to take these as the $E(\mathbf{K}, \mathbf{R})$ functions for these form N noncombining sets according to the value of \mathbf{K} . For convenience we shall take the zero of energy as the excitation energy ϵ_1 . Then the diagonal matrix elements are $\epsilon = \epsilon_0 - \epsilon_1$ for $\mathbf{R} = 0$, and zero otherwise. The nondiagonal elements may be made real by using the function $F(\mathbf{R}) = \exp i(\mathbf{K} \cdot \mathbf{R})E(\mathbf{K}, \mathbf{R})$. These elements are then β for states with \mathbf{R} differing by one lattice constant, zero otherwise. It is most convenient to number the states by the number of atoms the excited electron is separated from the ion, thus getting $F(0), F(1), \dots, F(N-1)$. If λ is an eigenvalue of the perturbation problem, and $\phi = a_0 F_0 + a_1 F_1 + \dots + a_{N-1} F_{N-1}$ is the eigenfunction, the equation $H\phi = \lambda\phi$ gives

$$\begin{aligned} (\lambda - \epsilon)a_0 &= \beta(a_{N-1} + a_1) \\ \lambda a_1 &= \beta(a_0 + a_2) \\ &\dots \dots \dots \\ \lambda a_{N-1} &= \beta(a_{N-2} + a_0) \end{aligned}$$

From the symmetry of the equations, it is seen that the solutions will be of two types: Odd, $a_r = -a_{N-r}$; even, $a_r = a_{N-r}$. The odd type leads to solutions of the form $a_r = \sin \alpha r$, where the range of distinct values of α is from 0 to π . The allowed values of α are thus $2\pi l/N$ where $l = 1, 2, \dots$, the largest integer $< N/2$. The values of λ are $2\beta \cos \alpha$. The even type solutions are of the form $a_r = \cos \alpha(r - N/2)$ with eigenvalues $\lambda = 2\beta \cos \alpha$. These values of a_r satisfy all equations save the first which gives the condition

$$(\lambda - \epsilon) \cos N\alpha/2 = 2\beta \cos(1 - N/2)\alpha.$$

Hence, we get the equation for α , $\epsilon/2\beta = -\sin \alpha \tan(N\alpha/2)$. For $E = 0$, this gives the same allowed α values and energy spectrum as the odd type. However, for $\epsilon \neq 0$ one of the roots in the range $0 \leq \alpha \leq \pi$ is lost and it is necessary to use complex values of α of the form $0 + i\gamma$ or $\pi + i\gamma$ to find it. Since the number of atoms is very large the values of $-\sin(i\gamma) \tan(i\gamma N/2)$ and $-\sin(\pi + i\gamma) \tan((\pi + i\gamma)N/2)$ may be simplified to $\sinh \gamma$ and $-\sinh \gamma$. The form of the

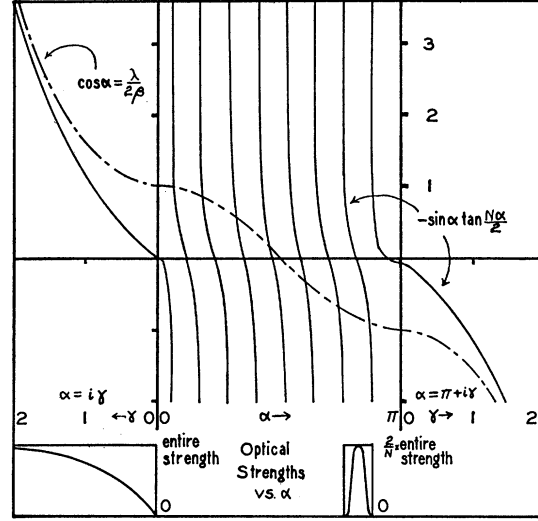


FIG. 5. Diagram for illustrating one-dimensional model. Abscissae of intersections of a horizontal line at ordinate $\epsilon/2\beta$ (where ϵ is energy difference between excitation and ionization energy at infinity, and 2β is width of Bloch band) and the curve $-\sin \alpha \tan N\alpha/2$ give values of α for the even states. The dotted curve gives energy λ , divided by 2β , as function of α . Lower diagrams give optical strength as function of α , the right-hand one for one of the states of the continuum, the left-hand one for the excitation state.

curve for this function for the various values of α is shown in Fig. 5. The allowed values of α are given by its intersections with a horizontal line whose ordinate is $\epsilon/2\beta$. The corresponding energies are $2\beta \cos \alpha$. The values of $\cos \alpha = \lambda/2\beta$ are also plotted. It is seen that the allowed values of α form a continuum with one separated state whose energy is given by $2\beta \cosh \gamma = 2\beta(1 + \sinh^2 \gamma)^{1/2} = ((2\beta)^2 + \epsilon^2)^{1/2}$. It is clearly this state which becomes the excitation wave for large distances, $\epsilon \gg 2\beta$, while the continuum is composed of the ionization waves. The energy spectrum of the continuum itself is almost independent of ϵ , the maximum shift in any level due to changes in ϵ being equal to the energy spacing in the continuum.

We can use the solution given above to estimate the relative strengths of light absorption from the normal state to the various excited states. As was shown in the text, there is no matrix component for electric current between the normal state and the ionization waves, the entire optical strength being concentrated in the excitation wave. If the optical strength of the excitation wave is taken as unity, then the optical strength of one of the new eigenfunctions $\phi = a_0 F_0 + a_1 F_1 + \dots$ is given by $|a_0|^2 / \sum |a_i|^2$. From the unitary property of the transformation to principal axes, it follows that the sum of these is always unity. The optical strength is seen to be zero for the odd states.

For the even states with α real it is $\cos^2(\alpha N/2) / \sum_{r=0}^N \cos^2 \alpha(r - N/2) = 2 \cos^2(\alpha N/2) / N$. For the separated state, for which α is complex, the strength is $\cosh^2(\gamma N/2) / \sum_{r=0}^N \cosh^2 \gamma(r - N/2) = \tanh \gamma$. For the case of large separation,

$\epsilon_0 - \epsilon_1 = \epsilon \gg \beta$, we see that γ is large and $\tanh \gamma \approx 1$. Hence the separated state is almost pure excitation wave and contains almost all the optical strength. For the states in the continuum $\tanh(\alpha N/2)$ must be large compared with unity so that $\cos(\alpha N/2) \ll 1$ and the strengths of these

states are small. The figure shows how the strengths depend upon the values of α . It is seen that even for the case where separation of the single state from the continuum is only 5 percent of the width of the continuum, it still possesses 40 percent of the optical strength.

OCTOBER 15, 1936

PHYSICAL REVIEW

VOLUME 50

The Infrared Absorption of Hydrogen Chloride in Nonionizing Solvents

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(Received August 3, 1936)

The infrared absorption of hydrogen chloride in four nonionizing solvents has been measured. In every solution studied the HCl fundamental vibrational frequency was found to be lower than for the gas. The variation in frequency was found to increase regularly with dipole moment of solvent when the solvents employed were of the same

chemical nature. Solvents of the benzene type were used, and it was found that the displacement of the 3.4μ band approached no limiting value even when a solvent of dipole moment 4.20×10^{-18} e.s.u. was used. The results obtained were attributed to the combined effects of dipole interaction and the formation of complexes.

THE infrared absorption spectrum of hydrogen chloride has been studied by a number of investigators, and the fundamental vibrational-rotational band has been observed at 3.46μ while the first harmonic has been found to appear at 1.76μ .¹ The rotational structure of both bands has been carefully studied. It has been of interest to determine the effects exerted upon the HCl molecules by neighboring units. Shearin² has studied the spectrum of solid HCl and reports the appearance of the fundamental at 3.74μ in this crystal with a series of broad rotational lines equally spaced about a zero line. In the case of solutions, Plyler and Williams³ have found the fundamental HCl frequency in benzene to be only slightly lower than in the gas but have reported their inability to detect any absorption arising from HCl molecules in aqueous solution, attributing the latter result to the high degree of dissociation of HCl in this solvent. Working with the Raman spectra of solutions of HCl in silicon tetrachloride, chloroform, sulphur dioxide, ethyl bromide, and acetyl chloride, West and Arthur⁴ found that the vibrational frequency of the solute decreased with increasing dipole

moment of solvent. These authors report that with solvents of low dipole moment the decrease in frequency is proportional to the dipole moment of the solvent. However, it appears that in the case of the solvents used by these authors there is a limiting variation in vibrational frequency of about 89 cm^{-1} produced by a solvent of moment 1.63×10^{-18} e.s.u., beyond which further increase in dipole moment is without effect. The solvent of highest dipole moment used in this study was acetyl chloride of moment 2.70×10^{-18} e.s.u. Subsequent infrared studies by West and Edwards⁵ on the effects of the same solvents on the harmonic near 1.76μ yielded results in agreement with the Raman work.

It was the purpose of the present investigation to determine the effects of another type of organic solvent on the HCl vibrational frequency in order to test the generality of the results obtained with the solvents mentioned above. It was desirable to use as solvents a series of compounds having similar chemical structures and having a wide range of dipole moments. Benzene, chlorobenzene, nitrobenzene, and *m*-nitrotoluene have dipole moments varying from zero in benzene to 4.20×10^{-18} e.s.u. in *m*-nitrotoluene and do not react chemically with HCl. The effects of these solvents on the HCl vibrational frequency was studied.

A Hilger infrared spectrometer with a fluorite

* Now at the University of Florida.

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