

to a value for  $\sigma$  of the order of  $10^{-3}$  nuclear units for  $W_r=5.2$ , an energy outside the range of validity of Eq. (12). The results of Breit and Condon<sup>7</sup> show that at this energy, the part of  $\sigma$  due to electric dipole transition is as large as that due to magnetic dipole, or perhaps somewhat larger. Utilizing this, the computed value of  $\sigma$  comes out to be about 0.005 nuclear units, in fair agreement with the experimental result.

### CONCLUSIONS

It has often been stated that the general characteristics of the interaction between neutron and proton are more or less independent of the shape of the field and of the size of the potential hole. We have shown, in a specific case which can be calculated by analytic means, that this is indeed the case. Once the constants are chosen so as to give the correct binding energy and elastic cross section for slow neutrons, the computed values of  $(1/\tau)$  and  $\sigma$  (for low energy photons) are insensitive to variation of the remaining parameters  $r_0$  and  $x_1$  within quite wide ranges of values of these parameters. Nor are the results particularly sensitive to the presence of a

Majorana exchange operator in the potential, or to whether there is a stable singlet state or not. Empirical determination of these properties will require the experimental measurement of quantities which depend more markedly on the angular momentum than do those discussed in the present paper.

The above result is a negative one, and as such is not particularly satisfying. However several positive conclusions can be drawn from our results. One is that the neutron-proton interaction must contain a term dependent on the coupling between the spins of proton and of neutron. Only in this way can be explained the large elastic cross section for slow neutrons, and the fact that the mean life of a slow neutron in the presence of protons is independent of its velocity, a property of magnetic dipole capture.

It is also apparent that the results are internally consistent: i.e., if one assumes that  $r_0$  is less than 0.8, that  $x_1$  is less than unity and that  $V_s$  is not equal to  $V_t$ , then a choice of parameters to fit two of the four bits of experimental data discussed above gives results which fit the other two experimental values.

## Electronic Energy Bands in Sodium Chloride

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The Wigner and Seitz method of cellular potentials has been applied to the calculation of wave functions in NaCl. A renormalized Hartree field has been used around the Cl and the Prokofjew field around the Na. The relative heights of the potentials are determined by use of Madelung's number. The problem of joining the functions at the cell boundaries has been treated by the Slater method of fitting  $\psi$  and  $\psi'$  at midpoints. For the outer Cl electrons a reasonable approximation is to join at Cl-Cl midpoints only. This gives rise to a face-centered lattice for which solutions of the Slater conditions have been found by

Krutter. Several new solutions have been derived which allow fairly accurate energy contours in momentum space to be drawn for the Cl  $3p$  band. If the joining is made at Cl-Na midpoints alone, a large number of unsatisfactory zero-width bands arise. When both Cl-Cl and Cl-Na midpoints are used, the boundary conditions can be treated only for special cases. For these they are consistent with the Cl-Cl solutions. Several attempts to calculate the ultraviolet absorption frequency are described and the difficulties involved are discussed.

### I. INTRODUCTION\*

THERE has been a great advance in the calculation of wave functions in solids in the last four years. The initial impetus was derived

from the contributions of Wigner and Seitz.<sup>1</sup> From a consideration of the Pauli principle they concluded that an electron in a monovalent metal

\* The writer is indebted to Dr. Seitz for discussions of this paper and that by Douglas H. Ewing and Frederick Seitz. The viewpoints of the two papers differ in that the

ionic picture of the lattice has been adhered to in this paper and no attempt to obtain a self consistent field has been made.

<sup>1</sup> Wigner and Seitz, *Phys. Rev.* **43**, 804 (1933).

is surrounded by a "Fermi hole" in the charge distribution of the other electrons. This hole has roughly the volume corresponding to one atom. When the electron is on one of the atoms in the lattice, it finds that the hole produces a net positive charge on that atom, while all other atoms are neutral and produce no field. The total potential for this electron is, thus, just that which it would experience about the same atom in the case of free atoms. If the field for the free atom is known, this picture gives the field in the metal. Since the field is spherically symmetrical about any atom, the wave equation can be separated in spherical harmonics and the radial functions obtained by numerical integration. The problem of utilizing the functions so obtained to construct Bloch type functions continuous in going from atom to atom was first discussed by Slater.<sup>2</sup> On the basis of this picture, calculations have been carried out for metallic Na,<sup>2</sup> Li,<sup>3</sup> Cu,<sup>4</sup> diamond,<sup>5</sup> LiH and LiF.<sup>6</sup>

In a later attempt to improve their values, Wigner and Seitz<sup>7</sup> consider their method from the viewpoint of the Fock equations. The Fock equation for one of the one-electron wave functions may be written in the form

$$[-(\hbar^2/2m)\nabla^2 - eV(r_i) - A_i(r_i)]\psi_i(r_i) = E_i\psi_i(r_i) \quad (1)$$

where  $V(r_i)$  is the coulomb potential of the combined positive and negative charges and

$$A_i(r_i) = (1/\psi_i(r_i)) \sum' i \int \psi_i^*(r) \times \psi_i(r) (e^2/|r-r_i|) dv \psi_i(r_i). \quad (2)$$

The  $\sum' i$  is to be taken over all occupied states of the same spin as  $\psi_i$ . In the case of free electrons, where the  $\psi$ 's are plane waves, the exchange term  $A_i$  is merely a constant which depends upon the momentum of the wave function  $\psi_i$ .<sup>8</sup> In the case of metallic sodium, the wave functions are near enough plane waves to warrant regarding the term as a constant there. For the case of a substance such as NaCl, the wave functions will be as near free atom Bloch functions as plane

waves, and the effect of  $A$  should be considered afresh. Consider Bloch functions of the form

$$\psi_{i,n}(r) = (1/\sqrt{N}) \sum_{\alpha} e^{2\pi i k_j \cdot R_{\alpha}} \psi_n(r - R_{\alpha}). \quad (3)$$

The  $N$  atoms of the lattice are located at the lattice points  $R_{\alpha}$  the index  $n$  refers to the atomic level and the allowed values of  $k_j$  are determined by periodicity requirements on the boundary of a large box. For these functions the summation over  $i$  in the  $A$  term can be readily worked out. It is found that if  $r_i$  is on atom  $\alpha$ ,  $A$  vanishes unless  $r$  is on atom  $\alpha$  also. Thus, so far as exchange is concerned, Eq. (1) reduces to the Fock equation for a single atom. This result could have been seen at once by realizing that the Bloch functions (3) are obtained from the single atom functions  $\psi_n(r - R_{\alpha})$  by a unitary transformation which does not mix free atom functions having different energy parameters  $E_n$ . Under these conditions the Fock equations will be satisfied in formally the same way by either set of functions.

Thus, for both the free electron functions and the atomic Bloch functions, the  $A$  term is interpretable as the potential due to a hole in the electron distribution which surrounds a given electron. For the free electrons the shape of the hole has no particular significance, but the potential due to it depends on the momentum or wave vector of the solution.<sup>8</sup> For the atomic Bloch functions, the hole for a given  $\psi_{i,n}$  in the  $\psi_n$  distribution is Hartree-like about a given atom (at least insofar as the Hartree approximation represents the Fock equations for one atom) and does not depend on  $k$ . Since in NaCl the ions are not very tightly squeezed together, we should expect the Hartree hole to be preferable to the Fermi hole.

## II. CALCULATION

The fields of the  $\text{Cl}^-$  ion have been computed by Hartree.<sup>9</sup> These were modified before use by renormalizing them so that all the  $3p$  and  $3s$  electrons were contained in a sphere whose volume was equal to the space over which these functions were expected to be large in the lattice. This was taken to be the volume belonging to a NaCl molecule less the volume of a spherical

<sup>2</sup> J. C. Slater, Phys. Rev. **45**, 794 (1934).

<sup>3</sup> J. Millman, Phys. Rev. **47**, 286 (1935).

<sup>4</sup> H. M. Krutter, Phys. Rev. **48**, 664 (1935).

<sup>5</sup> George E. Kimball, J. Chem. Phys. **3**, 560 (1935).

<sup>6</sup> Ewing and Seitz, Phys. Rev. (this issue).

<sup>7</sup> Wigner and Seitz, Phys. Rev. **46**, 509 (1934).

<sup>8</sup> John Bardeen, Phys. Rev. **49**, 653 (1936).

<sup>9</sup> D. R. Hartree, Proc. Roy. Soc. **A141**, 282 (1933).

Na<sup>+</sup> ion. The fields corresponding to the renormalized charge distributions were then calculated, and new *s* and *p* functions for a wide range of energy parameters were computed from them by Hartree's methods of numerical integration.<sup>10</sup> There are no *d* and *f* functions in Cl<sup>-</sup>, so the Hartree field for them was taken to be the same as for the *3p* functions, that is, the spherically averaged field of the configuration  $1s^2 2s^2 2p^6 3s^2 3p^5$  and the nucleus.

Since the valence electrons of Cl were expected to have small amplitude about the Na<sup>+</sup> ion, the hole about the Na was considered negligible and the field and wave functions there were taken to be the same as those in metallic sodium.<sup>11</sup>

Since the ions in NaCl are not neutral, the field due to the neighbors of any one ion must be considered. If this field is expanded in spherical harmonics, it will contain a constant term and terms in  $l=4, 6, 8$ , etc., which are neglected because they are much smaller than the constant term and average to zero in the spherical approximation. The value of the constant term can be obtained from Madelung's number which gives the electrostatic energy per cell (4 molecules) and consequently the potential at a lattice point of an ionic lattice in terms of the lattice constant and the charge on the lattice points. For the NaCl lattice this gives

$$\varphi_{Cl} = (13.94e^2/a) \div 4 \quad (4)$$

for the potential at a Cl<sup>-</sup> ion due to the other ions.<sup>12</sup> In atomic units this value is 0.66 for NaCl. Hence, if a wave function were obtained in the Hartree field of a Cl<sup>-</sup> ion less one *3p* electron (net charge zero) for a positive energy parameter  $\epsilon_C$ , then the total energy in the lattice for the same wave function would be  $\epsilon_L = \epsilon_C - 0.66$ . Similarly for Na<sup>+</sup> wave functions it would be  $\epsilon_L = \epsilon_N + 0.66$ .

Thus the charge distribution which produces the field in which the electron moves is that of the entire ionic lattice when the electron is on a Na ion, or else the same charge less that of

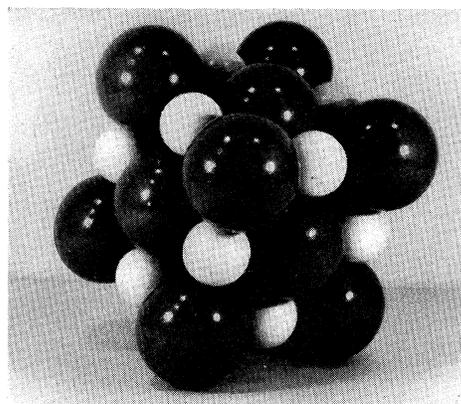


FIG. 1. Scale model of NaCl.

one electron on the Cl ion where the electron is. Physically it does not seem very plausible that the defect of one electron in the neighborhood of a given electron should vanish entirely when the electron moves from a Cl ion to a Na ion. To investigate this the exchange potential due to a two atom type Bloch function (see Eq. (6)) was calculated. This exchange potential has decidedly nonphysical properties. It is in general complex and, when averaged spherically, gives zero fields for the wave function with  $k=0$ . This peculiar behavior probably indicates a deficiency of the Fock-Bloch method of dealing with this case. A more sensible behavior of the hole when the electron moves onto a sodium would be for it to distribute itself onto the six surrounding Cl ions. This results in a lowering of the sodium potential by 0.38 At.U., so that  $\epsilon_L = \epsilon_N + 0.66 - 0.38 = \epsilon_N + 0.28$ . It was convenient to carry out calculations for  $\epsilon_L = \epsilon_N + 0.58$  at the same time, and the results for both are given in the next section.

### III. JOINING METHODS

On the basis of the ionic radii, it is seen that in NaCl the Na<sup>+</sup> and Cl<sup>-</sup> ions touch and the Cl<sup>-</sup> ions almost touch (Fig. 1). We are interested principally in the Cl<sup>-</sup>*3p* band. For this the wave functions will be much larger around the Cl than around the Na. Hence, the requirements of continuity will probably be as important in going from Cl to Cl as Na to Cl. Three different sets of continuity requirements were considered in all. These are classified according to the

<sup>10</sup> D. R. Hartree, Proc. Camb. Phil. Soc. 24, 89 (1928).

<sup>11</sup> The writer is indebted to Professor J. C. Slater for the use of his wave functions calculated in connection with reference 2.

<sup>12</sup> See the article by Born and Göppert-Mayer, *Handbuch der Physik*, XXIV/2, for a discussion of lattice potentials.

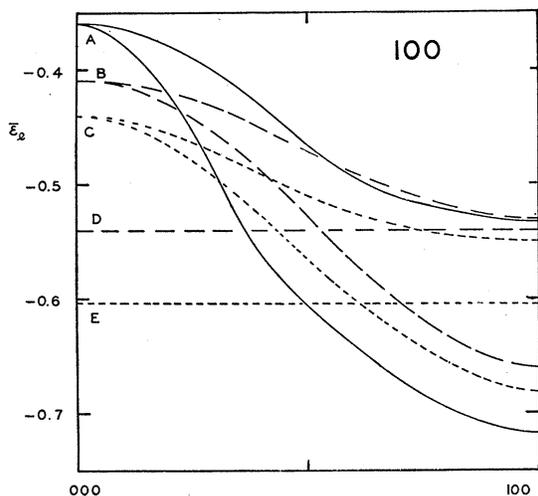


FIG. 2.

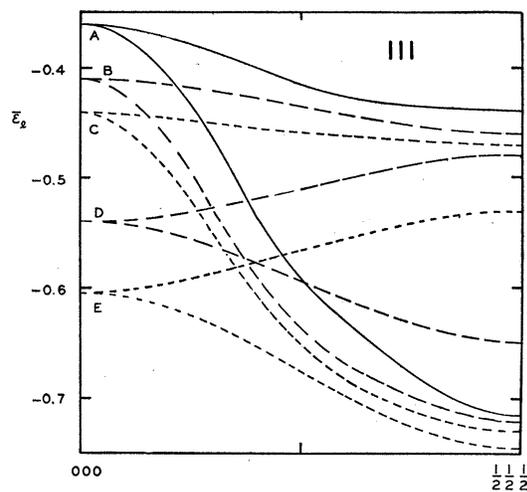


FIG. 3.

FIGS. 2 AND 3. Energy bands for the three joining conditions. ( $k$  space is body-centered and the scale has been chosen so the lattice points are 111, 200, etc.)

- A. Cl-Cl
- B. Cl-Cl-Na
- C. Cl-Cl-Na
- D. Na-Cl
- E. Na-Cl

$$\begin{aligned} \epsilon_L &= \epsilon_N + 0.58 \\ \epsilon_L &= \epsilon_N + 0.28 \\ \epsilon_L &= \epsilon_N + 0.58 \\ \epsilon_L &= \epsilon_N + 0.28 \end{aligned}$$

points at which the Slater conditions (continuity at the midpoint of an interatomic line of  $\psi$  and the component of  $\nabla\psi$  along the line) are fulfilled.

### 1. Cl-Cl

Neglecting the wave functions of the  $\text{Na}^+$  ions entirely, we are led to consider a face-centered lattice of  $\text{Cl}^-$  ions. The Slater conditions are required to be fulfilled at the Cl-Cl midpoints. For this lattice a suitable set of 12 wave functions (one  $s$  function, three  $p$ 's, five  $d$ 's, and 3  $f$ 's of the form  $x(y^2-z^2)/r^3$ ) have been found by Krutter.<sup>4</sup> He gives solutions for the particular directions 100, 110, 111 for  $k$ . The relationship between energy and  $k$  for the 100 and 111 lines are shown in Figs. 2 and 3. A sufficient set of further solutions have been obtained to allow rough interpolations to be made to general points in  $k$  space<sup>13</sup> (Fig. 4).

### 2. Na-Cl

For one type of atom in a lattice with centers of symmetry it can be proved that the wave function should be of the type

$$\psi_k(r) = \sum_{\alpha} e^{2\pi i k \cdot R_{\alpha}} [u_g(r-R_{\alpha}) + iu_u(r-R_{\alpha})] \quad (5)$$

<sup>13</sup> These new solutions are to be submitted to the *Physical Review* in the near future.

where  $u_g$  is an even real function of its vector argument and  $u_u$  is odd and real. Such functions materially simplify the setting up of the Slater conditions. If there are two types of atoms at centers of symmetry, as in NaCl, then the proper function is of the form of (5) summed over one set of atoms plus a precisely similar sum over the other set.

$$\begin{aligned} \psi_k(r) &= \sum_{\alpha} e^{2\pi i k \cdot R_{\alpha}} [u_g(r-R_{\alpha}) + iu_u(r-R_{\alpha})] \\ &+ \sum_{\beta} e^{2\pi i k \cdot R_{\beta}} [v_g(r-R_{\beta}) + iv_u(r-R_{\beta})]. \quad (6) \end{aligned}$$

If we consider a  $\text{Cl}^-$  ion as being at  $r=0$ , then it is surrounded by 6 Na ions at  $a(\pm\frac{1}{2}00)$ ,  $a(0\pm\frac{1}{2}0)$  and  $a(00\pm\frac{1}{2})$ . The continuity requirements at the Na-Cl midpoint  $a(\frac{1}{4}00)$  are

$$\begin{aligned} u_g + iu_u &= e^{\pi i k_x a} [v_g - iv_u], \\ u_g' + iu_u' &= e^{\pi i k_x a} [-v_g' + iv_u']. \quad (7) \end{aligned}$$

Here the functions are taken to be sums of surface harmonics times their corresponding radial functions. They are all evaluated for an argument of  $a(\frac{1}{4}00)$  and ' indicates  $\partial/\partial r$ . Separating real and imaginary parts, we see that each interface gives 4 conditions and the six interfaces would give 24 conditions in all.

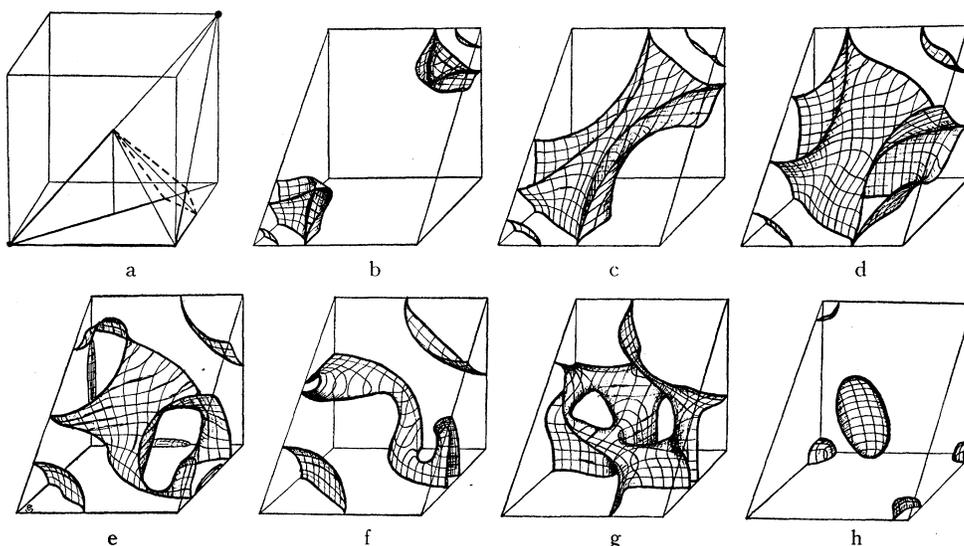


FIG. 4. Energy contours in  $k$  space for Cl-Cl. a, shows two lattice points in  $k$  space, and the elementary segment of the first Brillouin zone; b,  $\epsilon_L = -0.41$ ; c,  $\epsilon_L = -0.46$ ; d,  $\epsilon_L = -0.51$ ; e,  $\epsilon_L = -0.56$ ; f,  $\epsilon_L = -0.61$ ; g,  $\epsilon_L = -0.66$ ; h,  $\epsilon_L = -0.71$ .

However, for functions of type (6), the  $a(\frac{1}{4} 0 0)$  and  $a(-\frac{1}{4} 0 0)$  interfaces are equivalent and only 12 conditions are independent. Hence, if we expand the  $u$ 's and  $v$ 's in terms of 12 solutions of the spherical equations for the  $\text{Na}^+$  and  $\text{Cl}^-$  ions, the 12 homogeneous equations (for the expansion coefficients) will be soluble if, and only if, the determinant of the equations vanishes. This determinant is a function of  $k_x$ ,  $k_y$ ,  $k_z$  and the various radial functions and their derivatives. Since the latter are functions of the energy, the vanishing of the determinant gives a relationship between energy and momentum.<sup>14</sup>

The natural set of twelve functions to choose is an  $s$  function, three  $p$ 's, and two  $d$ 's of the form  $(x^2 - y^2)/r^2$  for each type of atom. Even for these simple functions, the determinant derived from the Eq. (7) proves to be more difficult to handle than the corresponding 12th order determinant of the face-centered lattice. Some results for calculations in the special directions 100 and 111 are shown in Figs. 2 and 3. In Fig. 3 the upper band is double; in Fig. 2 the "zero width" band is double and there is also a third band corresponding to the single band of Fig. 3, which is not shown. The dotted curves correspond to a total defect of one electron on the Cl's which surround the electron when it is on a Na, and the dashed curve to a lesser defect (see Section II).

<sup>14</sup> See reference 2 for a discussion of this method.

The reason the change of 0.3 in the Na potential produces only the small change 0.05 in the results is that the values lie within the Cl-3 $p$  band (the energy range for which  $p'/p < 0$ ). Within this band  $p'/p$  is a relatively sensitive function of the energy, while the corresponding quantities are much less sensitive for the  $\text{Na}^+$  wave functions. Hence, a change in the energy parameter of the latter can be compensated by a much smaller change in the former.

### 3. Cl-Cl-Na

The set of conditions derived by considering both Cl-Cl and Na-Cl midpoints simultaneously leads to twenty-four conditions, twelve of each type. Due to the complexity of this case, no attempt was made to choose a suitable set of functions. Instead, certain directions or points were chosen in  $k$  space and sets of functions were chosen in accordance with the symmetry groups for these points. Since the point  $k=0$  corresponds to full octahedral symmetry, only functions of the representation  $\Gamma_4$  (that of the Cl-3 $p$  functions) were used.<sup>15</sup> Similar considerations in connection with the other end points of Figs. 2 and 3 gave the results shown there. The dotted and dashed curves have the same significance as for the Na-Cl case.

<sup>15</sup> For a classification of spherical harmonics according to the representations of  $O_h$ , see H. Bethe. Ann. d. Physik **3**, 133 (1929).

## IV. COMPARISON OF RESULTS

We see that for all the cases considered, the width and location of the energy band is approximately the same. The Cl-Cl and Cl-Cl-Na are very similar and are both quite different from the Na-Cl. In the absence of any criterion for testing the validity of the various methods, it appears that the width and location of the energy band is probably nearly right and that the detailed structure is more like that of the Cl-Cl and Cl-Cl-Na than the Na-Cl.

## V. CONCERNING THE BINDING ENERGY

It does not appear practical to carry out this method far enough to calculate binding energies as is done in the case of metals. The reason for this is the presence of six valence electrons rather than one. This means that when the wave functions are calculated in the crystalline field, any change in the wave function gives a fivefold reaction on the field for which the wave function is calculated. Also, there is no adequate zero for the energy of the lattice. The energy values obtained by Hartree for the Cl<sup>-</sup> ion may be in error (due to neglect of exchange effects and polarization of the other electrons by any one) by an amount comparable with the binding energy of NaCl. If these errors are not independent of the lattice spacing, their variation may obscure the variation which gives the binding energy.

## VI. CONCERNING EXCITATION

One quantity which is generally supposed to be intimately connected with electronic bands in an insulator is the energy of excitation and the ultraviolet absorption. Under the influence of light, there will be a probability of excitation of an electron from a state in an occupied band to one in an unoccupied band. For ultraviolet light, the change in momentum of the electron will be negligible and the possible transition energies will be those for excitation without change of momentum. Absorption will become large when the energy of the light is equal to the least energy difference between states of the same momentum in an occupied and an unoccupied band.

There are rather serious difficulties in applying

the Fock method discussed in Section I to the calculation of excited states. The excitation of one electron will, of course, make an entirely negligible change in the field for an unexcited electron, so that the changes in the occupied states are inappreciable. However, the field acting on the excited electron is very different from that acting on one in a filled band. This is due to the orthogonality of the excited state wave functions to the filled state wave functions. Due to this orthogonality, the exchange potential for the excited electron will be very small, and the Fermi hole for it will be nearly negligible. From this we suspect that the Fock approximation is not as good for excited states as for the ground state and should be modified by a correlation between electrons of parallel spin, which would restore some of the lost hole.

An attempt to calculate the excitation energy on the basis of the three joining conditions used in III gave unsatisfactory results. The energy difference between the bands varied from about 3 times the experimental value (0.54 At.U.), when the hole was omitted for the excited state wave functions, to about  $\frac{1}{3}$ , when the hole was retained.

Also, the width (0.35 At.U.) of the lower band alone is roughly five times the width expected for the first absorption band for NaCl from the data of Hilsch and Pohl<sup>16</sup> and O'Bryan.<sup>17</sup> Since it is rather unlikely that the upper band should be such as to decrease the total spread for band to band transition, it does not appear possible that the electronic energy band picture can give the right behavior for absorption. There is a possibility that the detailed structure of the bands, causing a concentration large number of transition probabilities in certain energy ranges, could be responsible for the absorption peaks.<sup>18</sup> However, until more accurate work is done on the bands, this cannot be determined.

The writer wishes to acknowledge his indebtedness to Professor J. C. Slater for directing this research and to Professor P. M. Morse for the theory and practice of drawing space contours.

<sup>16</sup> R. Hilsch and R. W. Pohl, *Zeits. f. Physik* **59**, 812 (1930).

<sup>17</sup> H. M. O'Bryan, *Phys. Rev.* **49**, 944 (1936).

<sup>18</sup> Such peaks have been computed for the energy levels of Cu. E. Rudberg and J. C. Slater, *Phys. Rev.* **50**, 150 (1936).

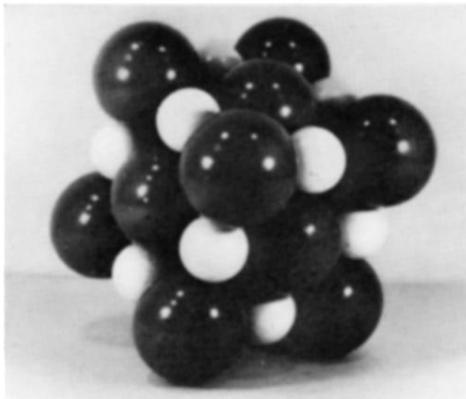


FIG. 1. Scale model of NaCl.