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On the Electronic Constitution of Crystals; LiF and LiH

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A self-consistent solution of the Hartree-Fock system of equations for the ionic crystals LiF and LiH is attempted using approximation methods previously employed in metals. In part *A* the boundary equations which the periodic functions must satisfy in the case of a face-centered cubic lattice are examined from the group theoretical standpoint. In part *B* the Hartree system of equations is solved using ion core fields which include the $(1s)^2$ electrons in both Li and F, so that eight electrons are given periodic functions in LiF and two in LiH. These solutions, which are regarded as preliminary ones, involve the use of the "*s* sphere approximation." The final results in both cases show that the Hartree approximation allows considerable charge to be in the vicinity of the metal ion so that the classical ion model is appreciably incorrect in that the valence electrons are not localized in a definite region about the electronegative atoms. The extent to which this affects the Born-Madelung lattice energy computations is discussed from the viewpoint of a complete solution.

It is the intention of this paper* to extend the schemes that are available at present for determining solid state electronic wave functions of the Bloch type, and to investigate the electronic structure of the ionic solids LiF and LiH. These extensions to the general procedure lie partly in the introduction of formal group theoretical methods into the schemes available for specifying the one-electron states, and partly in the use of particular simplifying steps in carrying through an approximate solution of Hartree's equations for solids. These developments are applied to the cases of the crystals mentioned above in order to obtain a better understanding of their constitution and to attempt to throw more light upon some of their characteristic optical and electronic properties.

Ionic crystals have been made the subject of a considerable amount of investigation from the classical atomic standpoint by Madelung, Born and others using semi-empirical methods, and this work has been successful in tying together various properties of these crystals such as compressibility, density and binding energy. On the other hand, there is convincing evidence to indicate that the simple ion model which forms a starting point for this development greatly oversimplifies the actual condition, and for this reason an investigation of such substances from the purely theoretical standpoint seems particularly appropriate. This topic will be discussed in later paragraphs, and we shall proceed with the discussion of the construction of wave functions after outlining the formal background.

PART A. GROUP THEORETICAL FOUNDATION

1. Reduction of space groups

The symmetry properties of crystals[1] are primarily characterized by the presence of a translation group (i.e., lattice structure). That is, the crystal is sent into itself by a set of translations of the type

$$t = n_1\tau_1 + n_2\tau_2 + n_3\tau_3 \tag{1}$$

where τ_1, τ_2, τ_3 are the primitive translations, which define the fundamental cell of the crystal, and the n's are integers. In addition, however, the crystal may have other symmetry operations which instead of being of the simple translational form

$$x_1' = x_1 + t_1, \quad x_2' = x_2 + t_2, \quad x_3' = x_3 + t_3, \tag{2}$$

corresponding to (1), where x_1', x_2', x_3' are the coordinates of the points x_1, x_2, x_3 after translation by means of $t = (t_1, t_2, t_3)$, are of the type

$$\begin{aligned} x_1' &= a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + a_1, \\ x_2' &= a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + a_2, \\ x_3' &= a_{31}x_1 + a_{32}x_2 + a_{33}x_3 + a_3. \end{aligned} \tag{3}$$

In this the crystal is to be regarded as rotated as well as translated, the rotation being de-

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* We wish to thank Dr. W. Shockley for valuable discussions in connection with his work on NaCl, which accompanies this paper, and ours.

[1] R. W. G. Wyckoff, *Structure of Crystals* (1931); F. Seitz, Zeits. f. Krist. **88**, 433 (1934), et seq.

scribed by means of the matrix

$$\alpha=\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{13} \\ a_{31} & a_{31} & a_{22} \end{pmatrix} \qquad (4)$$

and the translation by means of the vector

$$a=\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}. \qquad (5)$$

The complete symmetry of the crystal will be described by a group of transformations of type (3), and since the Hamiltonian operator will have this symmetry, it follows that all its eigenfunctions will belong to irreducible representations of this group in accordance with the fundamental theorem of Schur.[2] Since the total wave function of the normal state will belong to the unit representation, practically speaking (i.e., have the same symmetry as the crystal), we may conclude that the one-electron functions of the Hartree-Fock approximation will belong to particular representations of the space group.[3] This means, essentially, that the Hartree-Fock field acting on a given electron will have the symmetry of the lattice which is a self-consistent assertion.

Bloch[4] has shown that the translation group will be reduced if the coordinate system in the Hilbert space is defined by means of the set of functions

$$\psi_k=\chi_k e^{ik\cdot r} \qquad (6)$$

where χ_k is invariant under the translation group, and, using periodic boundary conditions,

$$k=\frac{n_1}{N}\frac{\tau_2\cdot\tau_3}{(\tau_1\tau_2\tau_3)} \qquad (7)$$

where n_1, n_2, n_3 are integers, N is the number of cells along an edge of the crystal block for which the periodic conditions are satisfied, and $(\tau_1\tau_2\tau_3)$ is the volume of the unit cell. Actually, the reduction of the translation group is never necessary since the complete group is always larger. This is true even in the triclinic case because of the time reversal symmetry of the Schrödinger equation.[5] Nevertheless it is convenient to use (6) because of its inherent simplicity. In this connection we may introduce the concept of a three-dimensional k space in the usual way. This is defined by the practically continuous set of points (7).

Regarding the problem of reducing the space groups, this has been formally carried through by one of us for all types of crystals.[6] In the present paper, however, we shall consider only those results of this investigation that refer to the simple type of space group in which all elements are of such a type that that a in (3) is a member of the group of translations (1). The simple face centered lattice of the NaCl type belongs to this set. Under these conditions the irreducible representations may be found as follows.

In k space, all of the functions of type (1) going with points k that are sent into one another by the g-order group G of the crystal class[7] acting at the origin of coordinates, $k=0$, will belong to a g-dimensional irreducible representation, unless two of the equivalent k's differ by a vector of "type K," where

$$K=l_1\frac{\tau_2\cdot\tau_3}{(\tau_1\tau_2\tau_3)}+l_2\frac{\tau_3\cdot\tau_1}{(\tau_1\tau_2\tau_3)}+l_3\frac{\tau_1\cdot\tau_2}{(\tau_1\tau_2\tau_3)}, \qquad (l_1,\, l_2,\, l_3=0,\, 1,\, 2\cdots). \qquad (8)$$

When this condition is met with, as it will be when one of the k's lies along a symmetry axis or plane or at a distance $K/2$ from a symmetry plane, etc., the irreducible representations are not g dimensional, but are generally lower. If we consider the set of $r=g/n$ equivalent k's which differ by vectors of type K (which belong to equivalent representations of the translation group) and the subgroup R of G which send these into one another, the theory asserts that only those linear combinations of this set which belong to an irreducible representation of R belong to an irreducible representation of the space group. The full set of g equivalent k's divide themselves

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[2] E. P. Wigner, *Gruppentheorie*, Vieweg (1931); H. Weyl, *Group Theory and Quantum Mechanics.*

[3] F. Seitz, Phys. Rev. **47**, 400 (1935).

[4] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

[5] E. P. Wigner, Nach Gött. Geo. (1932).

[6] F. Seitz, Annals of Math. **37**, 17 (1936).

[7] i.e., the factor group of the space group in which the translation group corresponds to the unit element, etc. g is 48 for crystals of type O^h.

into n sets containing r points which, like the foregoing set, go with $r\,\psi$'s that belong to equivalent representations of the translation group and which are sent into one another by an r-dimensional subgroup of G that is equivalent to R. If the first set of r functions is reduced with respect to R into irreducible representations, D_i, of dimensionality l_i (i runs over all irreducible representations of R), those functions in the other $n-1$ sets which belong to the equivalent irreducible representations of the corresponding group will join with the l_i functions of the first, going with D_i to form an nl_i-dimensional irreducible representation of the space group.

To summarize, if the $g\,\psi$'s equivalent to a given one do not all belong to different representations of the translation group, it is not sufficient that it be of the form (1) if it is to belong to an irreducible representation of the space group, but it is also necessary (and sufficient) that it belong to an irreducible representation of the group R which connects it into those $r-1$ of the g functions which belong to equivalent representations of the translation group.

It is to be emphasized that this statement is valid only for the simple types of space group specified above. The situation is more complicated for crystals of the beryllium and diamond type in which screw motions occur.

From this standpoint it is possible to draw several important conclusions[8] concerning the nature of the energy surface in K space, and for the purpose of the discussion we shall employ the reduced zone scheme in which points of k space which differ by a vector K are regarded as identical, so that we view the energy function as a many-valued function in the first zone, that is as a set consisting of many three-dimensional surfaces. At most points in this first zone the energy surfaces will be separated because the functions going with the point k will belong to different or equivalent representations of the space group, and the energies of these tend to repel one another. At certain points along symmetry axes or at the point $k=0$, however, some of the surfaces will touch one another because several functions which belong to equivalent representations of the translation group belong to the *same* representations of the space group, for reasons we have outlined above, and must have the same energy. We shall consider practical cases of this later in connection with the face centered cubic crystals.

If one goes to an extended zone picture, instead of the reduced one, in which the energy surface is taken to be single valued, the existence of contact between some of the surfaces in the multiple surface picture of the latter scheme will reflect itself in the absence of discontinuities of the energy surface at certain points of some of the zones or even at entire lines. In the zone space of the face-centered lattice, the eight cube corners

$$\begin{pmatrix}\pm 1/2a\\ \pm 1/2a\\ \pm 1/2a\end{pmatrix}$$

are of this character, where $2a$ is the length of the edge of the fundamental cube of the crystal lattice.

A very interesting behavior occurs when we get far enough from the origin so that there is an equivalent point which differs by a K vector that is not zero. (Such points will only occur at the boundary of the zone if the Brillouin construction has been used.) We may regard the g-dimensional representation as breaking up into a number of smaller dimensional ones (if a symmetry plane or the time reversal operator has caused this, the number will be two) which insures us that there will be a gap at this point between the different surfaces. If this occurs at all points of the surface of the first zone it may be said to be specified by symmetry.[9] This is true of the cube of the simple cubic lattice, the rhombic dodecahedron of the body centered

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[8] L. P. Bouckaert, R. Smoluchowski and E. Wigner, Phys. Rev. **50**, 58 (1936), have considered similar problems from essentially the same viewpoint.

[9] It is to be kept in mind that we have adopted the convention that the points of k space are so chosen that those going with the same representation are equidistant from the origin, that is, are of equal length, and are sent into one another by the symmetry operation in such a way that k space undergoes a *rigid rotation* (i.e., there are no dilatations or other distortions). If only this restriction is made, the Brillouin zone scheme is not unique in the specification of zones, but rests only upon a perturbation scheme in which free waves are used in the starting approximation. If another starting scheme is used, a different set of zones will generally be met with, even when the foregoing convention is used. A small number of zones are uniquely specified by symmetry, however, and all schemes of construction will lead to these.

lattice, or the hexagonal prism of the hexagonal lattice Γ_h, in cases in which the symmetry class is $D_6{}^h$. On the other hand, only the center points of the hexagonal faces of the truncated octahedron of the face-centered lattice are specified by symmetry (the square faces are completely specified). This means that it is not necessary to use these plane surfaces as zone boundaries, but any other (curved) surfaces which join the center point and the square faces could be employed as long as surfaces on opposite sides of the figure are parallel and the cubic symmetry is maintained. Actually, of course, the Brillouin construction is the simplest to use in this particular case, but this is not always true, particularly in crystals of low symmetry. (The second zone in the hexagonal lattice in such a case.)

2. The construction of solid state wave functions

The plan which we shall use in specifying solid state wave functions will be essentially that employed heretofore in other cases[10] with the addition of the concepts discussed in Section 1. We shall assume that the potential field within the lattice is spherically symmetric about each atom and use such a field within the polyhedron surrounding each atom which is determined by planes that cut the lines joining nearest neighbors orthogonally. In the case of LiF, we may choose these planes in a number of independent ways because the Li and F atoms are not symmetrically equivalent as in most of the simple monoatomic lattices. Nevertheless, we shall select them so as to bisect the lines joining neighbors, thus giving a system of space filling cubes which are of equal size and surround each atom. The reason for this choice lies in the fact that closed shell electrons of the Li ion[11] just fit into such a cube without extending outside appreciably, while a smaller cell about these atoms would not be able to contain all of this charge distribution. On the other hand, it seems reasonable to use as large a region for the F atom since the fluorine field is very strong near the nucleus, so that the use of cubes seems to be a reasonable choice. Similar comments cover the LiH case.

Within these cubes, we shall assume that the eigenfunctions may be expanded into a series of surface harmonics $\theta_m{}^l$ with radial-function coefficients $f_l(r)$ which satisfy the Schrödinger equation in which the spherically symmetric part of the field going with the polyhedron occurs. That is,

$$\psi_k{}^{(0)}=\sum_{l,\,m} a_{lm}{}^{(0)} f_l(r)\theta_m{}^l \tag{9}$$

within the polyhedron where the a s are constants. Not all surface harmonics will necessarily appear in this expansion, but only those which are compatible with the representation of the space group to which the function ψ_k belongs. To be more explicit, we shall discuss the LiF lattice. Suppose that we choose the origin of coordinates so that an F atom is situated there. We may then choose the phase of the wave function under discussion so that

$$\psi_k=\psi_{e(o)}+i\psi_{o(o)} \tag{10}$$

where $\psi_{e(o)}$ is a real even and $\psi_{o(o)}$ a real odd function relative to an inversion in the origin, ι_o. If the k vector going with ψ belongs to a 48 rowed representation, there will be no limitation upon the surface harmonics which enter in (9) and ψ_e and ψ_o in (10) will contain all even and odd harmonics, respectively. If, however, the k goes with a representation of lower order, the harmonics which appear are restricted to the set belonging to a particular representation R (see Section 1) which sends the equivalent k's that differ by K vectors into one another. At the point $k=0$, for example, the only functions which appear in a given case must belong to the same representation of O^h. In other words, (9) must be of the form

$$\psi_k{}^{(0)}=\sum_l b_l{}^{(0)} f_l(r) A_j{}^l \tag{11}$$

where $A_j{}^l$ is a harmonic of order l going with a particular representation of R. If the phases are chosen in accordance with (10), the b's going with even l will be purely real numbers, and those going with odd l will be imaginary. We shall determine the b_l's which occur in (11) by the conditions, (a), that this ψ_k join on continuously with the similar function in each of the neighboring polyhedra and (b) that at points on opposite sides of the unit cell which are

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[10] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); J. C. Slater, Phys. Rev. **45**, 794 (1934), etc.

[11] Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1928).

separated by primitive translation distances τ_i ($i=1, 2, 3$), the phase of ψ_k differs by $e^{ik\cdot\tau_i}$.

If the neighboring cell is centered about the atom at a point r_n, the corresponding function will not be an even function plus i times an odd one as long as (10) is taken as the basis for choice of phase referring to inversion ι_n at the point r_n, but will be a constant times this. We know, however, that

$$\iota_o=\iota_n-2r_n \tag{12}$$

where $2r_n$ a translation of magnitude twice the distance r_n which is always an allowed translation, so that the form must be

$$\psi_k^{(n)}=e^{ik\cdot r_n}(\psi_{e(n)}+i\psi_{o(n)}) \tag{13}$$

where $\psi_{e(n)}$ and $\psi_{o(n)}$ are even and odd real functions relative to the inversion ι_n.

In a similar way, using equation of type (12), we may find the representation of the group R, operating about r_n, to which ψ_k must belong if it belongs to a given representation of the group R acting about the origin. We shall discuss practical examples of this later. Knowing this representation, we may determine the allowable harmonics which enter into the expansion in the polyhedron about r_n, so that we have

$$\psi_k^{(n)}=e^{ik\cdot r}\sum_l b_l^{(n)}f_lA_j \tag{14}$$

where the $b_l^{(n)}$ are purely real or purely imaginary depending upon whether l is even or odd.

Since all F atoms are equivalent, as are all Li atoms, the b's going with a given function will be the same for all F cells and for all Li cells, so that we need consider but two independent sets. Actually, we shall not consider an infinite number of these, but will only deal with a finite number going with the lowest order coefficients, using the conditions (a) and (b) discussed in a preceding paragraph of this section. This restriction to a finite number of terms rests, of course, upon practical limitations since we have not felt it feasible to solve determinants of higher than the eighth order. This procedure would be accurate only if independent methods of determining the coefficients led to essentially the same results. Actually, the error involved in the case of LiF is not negligibly small for the excited states.

In addition to using a small number of coefficients, we have introduced the "s sphere simplification" into the present paper. In this the fundamental polyhedron (a cube in our case) is replaced by a sphere of equal volume and the boundary conditions are satisfied at the surface of this rather than at the surface of the actual polyhedron. The approximation is not as good in this case as in that of the alkali metals, where its use could be rigorously justified, but the error it introduces is undoubtedly smaller than others, such as that discussed in the last paragraph, so we shall not hesitate to use it in this semi-quantitative investigation. In later work with LiH, in which we intend to strive for quantitative accuracy, we shall avoid its use and obtain a comparison with the present results.

We shall now proceed with a discussion of the determination of the boundary equation.

3. Boundary equations

No fixed rules regarding the points at which boundary conditions were satisfied were made. Generally speaking, points situated at prominent symmetry positions were used, except in cases in which these did not lead to a satisfactory specification (i.e., the secular equation vanished identically or leads to too simple an equation). Such cases indicate that the series (9) do not converge rapidly at these points so that new points were used. The equations derived in the following paragraphs cover k values in the three prominent symmetry directions, namely the (100), (111) and (110) directions, which will be discussed separately. Only two or three points on each of the energy surfaces going with these directions were determined and enough equations were obtained to discuss the filled and first empty band in LiF. Only one band is filled in LiH, so that all of the equations are not important for this case. We shall refer only to LiF in the discussion, but with the understanding that the results will be used for LiH as well.

I. $k=0$

For the case $k=0$, the basic symmetry requirement on the functions going with both of the polyhedra is that they belong to irreducible representations of the group[12] O^h. Since the lowest valence electron levels are s levels (considering the $(2s)^2$ $(2p)^5$ configuration on F and

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[12] We are here employing Bethe's notation, Ann. d. Physik 3, 133 (1929).

the $2s$ on Li and H), it is obvious that the lowest lattice function will be determined by Γ_1. The next will be Γ_4 because this is the analog of the p representation of spherically symmetric fields. This representation is triply degenerate, whence we may expect three energy surfaces to come in contact at $k=0$ to give a band capable of holding six of the eight electrons going with each unit cell of LiF. The other two electrons in this case, and the only two for LiH, will occupy the low "Γ_1 band." As we shall show later, the third, unoccupied band, is also Γ_1 at $k=0$.

(a) Γ_1. The prominent spherical harmonics which belong to Γ_1 are the s and g functions

$$1, \quad x^2y^2+y^2z^2+z^2x^2-(1/3)(x^4+y^4+z^4),$$

respectively. The angular functions which enter into both the Li and F expansions are the same in this case because $e^{ik\cdot\tau}=1$ for all τ's. It turns out that the use of the s sphere approximation excludes the appearance of the g function if prominent points are employed. The equations s functions must satisfy are

$$F(s)=L(s), \quad F'(s)=-L'(s) \tag{15}$$

where $F(s)$, $L(s)$ are the values of the radial s functions for F and Li at the boundary of the s sphere. The compatibility equation for (15) is

$$\frac{F'(s)}{F(s)}=-\frac{L'(s)}{L(s)}. \tag{15a}$$

(b) Γ_4. For Γ_4 the most important spherical harmonics are the p and f functions

$$p:\quad x,\ y,\ z$$

$$f:\quad x\left(x^2-\frac{3}{2}(y^2+z^2)\right),\quad y\left(y^2-\frac{3}{2}(z^2+x^2)\right),$$

$$z\left(z^2-\frac{3}{2}(x^2+y^2)\right)$$

of which we may select x and $x\left(x^2-\frac{3}{2}(y^2+z^2)\right)$ as belonging to the same row of equivalent representations. The boundary conditions were satisfied at the points (100) and (-100) for neighboring Li and F atoms, and for neighboring F atoms in the (110) direction at the points $(1/\sqrt{2},\ 0,\ 1/\sqrt{2})$ and $(-1/\sqrt{2},\ 0,\ 1/\sqrt{2})$. In addition, the derivative in the x direction was made continuous at the points (001) and $(00-1)$ for neighboring Li and F atoms in the (001) direction. The equations are

$$\begin{gathered}F(p)+F(f)=-L(p)-L(f)\\ F'(p)+F'(f)=L'(p)+L'(f)\\ -F(p)+\frac{1}{2}F(f)=0\\ F(p)-\frac{3}{2}F(f)=L(p)-\frac{3}{3}L(f)\end{gathered} \tag{16}$$

in the order mentioned above. The compatibility equation is

$$\frac{5}{2}\frac{F'(p)}{F(p)}+5\frac{F'(f)}{F(f)}+\frac{13}{2}\frac{L'(p)}{L(p)}+\frac{L'(f)}{L(f)}=0. \tag{16a}$$

II. Limiting point of (100) direction

The group R (see Section 1) going with the point $(k)=1/2a$ at the boundary of the zone in the (100) direction is $D_4{}^h$ which has five even and five odd representations. The character system of the classes of rotations of determinant 1 is as follows.

	E	C_2	C_4	C_2'	C_2''
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	1	1	-1	1	-1
Γ_4	1	1	-1	-1	1
Γ_5	2	-2	0	0	0

where

E is the unit element
C_2 is the twofold rotation about the x axis
C_4 is the fourfold rotation about the x axis
C_2' and C_2'' are twofold axes at right angles to these.

It is readily seen that the representation about the Li and F atoms will be identical by considering nearest neighbors in the x direction. The rotation about the x axis leaves both centers fixed, while the reflection planes ρ_{F} and ρ_{Li} and the twofold rotations δ_{F} and δ_{Li} satisfy the relation

$$\rho_{\mathrm{F}}=\rho_{\mathrm{Li}}+\tau, \quad \delta_{\mathrm{F}}=\delta_{\mathrm{Li}}+\tau,$$

where τ is the primitive translation in the x direction of magnitude $2a$, for which

$$K\cdot\tau=2\pi.$$

Since there is no possibility that the widely separated lower bands of the halides will cross one another, it seems natural to expect that the lowest will have a point going with the unit representation (Γ_1) at this limit point. Similarly, it seems natural to expect the second band to split into Γ_2 and the doubly degenerate Γ_5, because Γ_4 of O^h contains these two. We shall consider each of these cases.

(a) Γ_1. The simplest functions belonging to Γ_1 are

$$s:\ 1,\quad d:\ (y^2+z^2-2x^2)$$
$$g:\ x^2y^2+y^2z^2+z^2x^2-\tfrac{1}{3}(x^4+y^4+z^4).$$

Boundary conditions were satisfied between Li and F polyhedra neighboring in the x direction at the points (100) and (-100) and between neighboring cells in the y and z directions at (010), $(0-10)$ and (001), $(00-1)$, respectively. Only the s and d functions are needed for this and the resulting equations are

$$\begin{aligned}F(s)-2F(d)&=-L(s)-2L(d),\\ F'(s)-2F'(d)&=L'(s)-2L'(d),\\ F(s)+F(d)&=L(s)+L(d),\\ F'(s)+F'(d)&=L'(s)-L'(d).\end{aligned}\tag{17}$$

The secular equation reduces to

$$9\left(\frac{F'(s)}{F(s)}\frac{F'(d)}{F(d)}+\frac{L'(s)}{L(s)}\frac{L'(d)}{L(d)}\right)+8\left(\frac{F'(s)}{F(s)}\frac{L'(s)}{L(s)}+\frac{F'(d)}{F(d)}\frac{L'(d)}{L(d)}\right)+\left(\frac{F'(s)}{F(s)}\frac{L'(d)}{L(d)}+\frac{F'(d)}{F(d)}\frac{L'(s)}{L(s)}\right)=0.\tag{17a}$$

(b) Γ_2. Γ_2 is represented by

$$p:\ x,\quad f:\ x\left(x^2-\frac{3}{2}(y^2+z^2)\right).$$

The function and derivatives were taken to be continuous at the (100) and (-100) points for unlike neighbors in the x direction, and neighboring F functions were made continuous at $(1/\sqrt{2}\ 0\ 1/\sqrt{2})$ and $(-1/\sqrt{2}\ 0\ -1/\sqrt{2})$. In addition, the tangential gradients at (010) and $(0-10)$ for unlike neighbors in the (010) direction were made equal. The resulting equations are

$$\begin{aligned}F(p)+F(f)&=L(p)+L(f),\\ F'(p)+F'(f)&=-L'(p)-L'(f),\\ F(p)-\frac{1}{4}F(f)&=0,\\ F(p)-\frac{3}{2}F(f)&=L(p)-\frac{3}{2}L(f).\end{aligned}\tag{18}$$

The secular equation is

$$\frac{5}{4}\frac{F'(f)}{F(f)}\frac{F'(p)}{(Fp)}+\frac{1}{4}\frac{F'(f)}{F(f)}\frac{L'(p)}{L(p)}+\frac{F'(p)}{F(p)}\frac{L'(f)}{L(f)}=0.\tag{18a}$$

(c) Γ_5. For the doubly degenerate state Γ_5, we took

$$p:\ z,\quad f:\ z\left(z^2-\frac{3}{2}(x^2+y^2)\right)$$

and joined these, with continuous slope and derivative, to unlike neighbors in the z direction at the center of the square faces. In addition, the tangential gradient at the centers of the other faces were made continuous with those of the other unlike neighbors. These equations are

$$\begin{aligned}F(p)+F(f)&=L(p)+L(f),\\ F'(p)+F'(f)&=L'(p)+L'(f),\\ F(p)-\frac{3}{2}F(f)&=L(p)-\frac{3}{2}L(f),\\ F(p)-\frac{3}{2}F(f)&=-L(p)+\frac{3}{2}L(f)\end{aligned}\tag{19}$$

$$\text{or}\quad \frac{3}{2}\frac{F'(p)}{F(p)}+\frac{F'(f)}{F(f)}=-\left(\frac{3}{2}\frac{L'(p)}{L(p)}+\frac{L'(f)}{L(f)}\right).\tag{19a}$$

III. Midpoint of (100) direction

The group R associated with the point

$$k=\begin{pmatrix}114a\\0\\0\end{pmatrix}$$

midway from the origin to the boundary of the zone in the (100) direction is amply $C_4{}^v$ which is generated by a fourfold axis in the x direction and a plane passing through this. There are five representations for which the character system is

	E	C_2	C_4	R_v	R_v'
Γ_1	1	1	1	1	1
Γ_2	1	1	-1	-1	1
Γ_3	2	-2	0	0	0
Γ_4	1	1	1	-1	-1
Γ_5	1	1	-1	1	-1

R_v and R_v' stand for the two classes of reflecting planes which pass through the x axis. The representation will be the same for both atoms in a given case since the line joining nearest neighbors is either parallel to the symmetry axis or perpendicular to it.

Just as in the preceding case, we may conclude safely that the function associated with the lowest energy surface goes with Γ_1. The representation Γ_4 of O^h contains both this and Γ_3, which is doubly degenerate, so that it may be expected that the former will go with the same surface as Γ_2 of $D_4{}^h$ and the latter will go with the same two surfaces corresponding to Γ_5 of this group. In other words, two of the three energy surfaces of the second band remain in contact along the entire (100) axis.

(a) Γ_1. Functions which belong to Γ_1 are

$$s:\ 1,\quad p:\ x,\quad d:\ 2x^2-(y^2+z^2),$$
$$f:\ x\left(x^2-\frac{3}{2}(y^2+z^2)\right)$$

and all of these were used for either one state or the other. The boundary conditions employed were:

(A) Lowest band, using s, p, d functions

(1) Continuity of functions and derivative at the center of the square face joining neighboring unlike atoms in the x direction. The equations obtained from this are

$$\begin{aligned} F(s)+2F(d)-iF(p) &= -i[L(s)+2L(d)+iL(p)], \\ F'(s)+2F'(d)-iF'(p) &= i[L'(s)+2L'(d)+iL'(p)]. \end{aligned} \tag{20}$$

(2) Continuity of function and derivative at center of square face between nearest neighbors in the y (and z) directions

$$\begin{aligned} F(s)-F(d) &= L(s)-L(d), \\ F'(s)-F'(d) &= -L'(s)+L'(d). \end{aligned} \tag{20a}$$

The secular equation associated with these equations may be reduced to

$$\begin{vmatrix} \dfrac{F'(s)}{F(s)}+\dfrac{L'(p)}{L(p)} & 2\left(\dfrac{F'(d)}{F(d)}+\dfrac{L'(p)}{L(p)}\right) & 0 \\ \dfrac{L'(s)}{L(s)}+\dfrac{F'(p)}{F(p)} & 2\left(\dfrac{L'(d)}{L(d)}+\dfrac{F'(p)}{F(p)}\right) & 3\left(\dfrac{F'(p)}{F(p)}+\dfrac{L'(s)}{L(s)}+\dfrac{2L'(d)}{L(d)}\right) \\ \dfrac{F'(s)}{F(s)}+\dfrac{L'(s)}{L(s)} & -\left(\dfrac{F'(d)}{F(d)}+\dfrac{L'(d)}{L(d)}\right) & \dfrac{L'(s)}{L(s)}-\dfrac{L'(d)}{L(d)} \end{vmatrix}=0$$

(B) Second Band, using s, p and f functions

(1) Continuity at same point as in (1) of A:

$$\begin{aligned} F(s)-i[F(p)+F(f)] &= -i\{L(s)+i[L(p)+L(f)]\} \\ F'(s)-i[F'(p)+F'(f)] &= i\{L'(s)+i[L'(p)+L'(f)]\}. \end{aligned} \tag{21}$$

(2) Continuity of the tangential gradient at the point mentioned in (2) of A:

$$F(p)-\frac{3}{2}F(f)=L(p)-\frac{3}{2}L(f). \tag{21a}$$

(3) Continuity of the function at the point $(0\ 1/\sqrt{2}\ 1/\sqrt{2})$ and $(0\ -1/\sqrt{2}\ -1/\sqrt{2})$ for nearest like

neighbors in the (011) direction.

$$\begin{vmatrix} \dfrac{F'(s)}{F(s)}+\dfrac{L'(p)}{L(p)} & -\dfrac{3}{2}\left(\dfrac{F'(s)}{F(s)}+\dfrac{L'(p)}{L(p)}\right) & \dfrac{5}{2}\dfrac{F'(s)}{F(s)}+\dfrac{3}{2}\dfrac{L'(p)}{L(p)}+\dfrac{L'(f)}{L(f)} \\ \dfrac{F'(p)}{F(p)}+\dfrac{L'(s)}{L(s)} & \dfrac{F'(f)}{F(f)}+\dfrac{L'(s)}{L(s)} & 0 \\ 1-\dfrac{1}{\surd 2} & \dfrac{1}{4\surd 2}-\dfrac{3}{2} & \dfrac{5}{2} \end{vmatrix}=0 \tag{21b}$$

(b) Γ_3. Three functions belonging to Γ_3 are

$$p: y;\quad d: xy;\quad f: y\left(y^2-\frac{3}{2}(z^2+x^2)\right).$$

The conditions a linear combination of these was made to satisfy were

(1) Continuity, with unlike neighbors in x direction at the point $(1/\surd 2\ 1/\surd 2\ 0)$:

$$\frac{i}{\surd 2}F(p)+\frac{1}{2}F(d)-\frac{i}{4\surd 2}F(f)=\left(\frac{i}{\surd 2}L(p)-\frac{1}{2}L(d)-\frac{i}{4\surd 2}L(f)\right). \tag{22}$$

(2) Continuity of the gradient in the x and y directions at the same points

$$\begin{aligned} &\frac{1}{\surd 2}\left(i\frac{F'(p)}{\surd 2}+\frac{F'(d)}{2}-i\frac{F'(f)}{4\surd 2}\right)-i\frac{F(p)}{2}-i\frac{9}{8}F(f) \\ &\qquad =-\frac{i}{\surd 2}\left(i\frac{L'(p)}{\surd 2}-\frac{L'(d)}{2}-i\frac{L'(f)}{4\surd 2}\right)+i\left(i\frac{L(p)}{2}+\frac{L(d)}{\surd 2}-i\frac{3}{8}Lf\right), \\ &\frac{1}{\surd 2}\left(i\frac{F'(p)}{\surd 2}+\frac{F'(d)}{2}-i\frac{F'(f)}{4\surd 2}\right)+i\frac{F(p)}{2}+i\frac{9}{8}F(f) \\ &\qquad =\frac{i}{\surd 2}\left(i\frac{L'(p)}{\surd 2}-\frac{L'(d)}{2}-i\frac{L'(f)}{4\surd 2}\right)+i\left(i\frac{L(p)}{2}+\frac{L(d)}{\surd 2}-\frac{3L(f)}{8}\right). \end{aligned} \tag{22a}$$

IV. Endpoint of (111) direction

The group R going with

$$k=\frac{2\pi}{4a}\begin{pmatrix}1\\1\\1\end{pmatrix}$$

at the endpoint of the (111) axis is D_i^3, and the irreducible representations have the character system

	E	C_3	C_2
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

C_3 and C_2 correspond to the classes of threefold rotations about the (111) axis and twofold rotations at right angles to this respectively. Since the inversion is present, it is implied that the three classes of operators of determinant -1 have either an even or an odd character system.

If we consider two neighboring unlike atoms in the x direction, say an F at the origin and a Li at $-a$, the phase of the latter, relative to the former, is $-i$. A simple computation shows the following correction between the representations of the classes E, C_3, C_2 and I (inversion) for the two atoms.

$$E_{\mathrm{L}}=E_{\mathrm{F}},\quad C_{3\mathrm{L}}=C_{3\mathrm{F}},\quad C_{2\mathrm{L}}=-C_{2\mathrm{F}},\quad I_{\mathrm{L}}=-I_{\mathrm{F}}$$

where the subscript indicates the atom involved. In other words, if the representation going with the F polyhedron is Γ_1, even, that about Li will be Γ_2 odd; if that about F is Γ_3 even, that about Li will be Γ_3 odd; etc.

It seems reasonable to expect the lowest state to be Γ_1 even for F and Γ_2 odd for Li (and similarly for H and Li in LiH) since the F plays the most important role in the states of the lowest band. Γ_4 of O^h breaks into Γ_2 and Γ_3, the latter being doubly degenerate, and we have drawn the conclusion that the two (111) endpoints in the second band are:

F : Γ_2 odd, Li : Γ_1 even,

F : Γ_3 odd, Li : Γ_3 even.

(a) F : Γ_1 even, Li : Γ_2 odd.

The Γ_1 even functions used were

$$s:\ 1.;\quad d:\ xy+yz+zx$$

$$g:\ x^2y^2+y^2z^2+z^2x^2-\tfrac{1}{3}(x^4+y^4+z^4)$$

while the Γ_2 odd were

$$p:\ x+y+z,$$

$$f_1:\ x\left(x^2-\frac{3}{2}(y^2+z^2)\right)+y\left(y^2-\frac{3}{2}(x^2+z^2)\right)+z\left(z^2-\frac{3}{2}(x^2-y^2)\right),$$

$$f_2:\ xyz.$$

(1) The continuity condition at the point (100) and (−100) between neighbors in the x direction give

$$F(s)-\tfrac{1}{3}F(g)=L(p)+L(f_1),\quad F'(s)-\tfrac{1}{3}F'(g)=-L'(p)-L'(f_1). \tag{23}$$

(2) Continuity of the y (and z) gradient for the point considered in (1) yields

$$-F(d)=L(p)-\frac{3}{2}L(f_1). \tag{23a}$$

(3) Continuity between the same neighbors at the points $(-1/\sqrt{3}\ 1/\sqrt{3}\ 1/\sqrt{3})$ and $(1/\sqrt{3}\ 1/\sqrt{3}\ 1/\sqrt{3})$:

$$F(s)+F(d)+\frac{2}{9}F(g)=-\frac{1}{\sqrt{3}}\left(L(p)-\frac{2}{3}L(f_1)-\frac{1}{3}L(f_2)\right). \tag{23b}$$

(4) Continuity of the x and y gradient at the same point.

$$\begin{aligned}\frac{1}{\sqrt{3}}\left(F'(s)+F'(d)+\frac{2}{9}F'(g)\right)&=\frac{1}{\sqrt{3}}\left(\frac{1}{\sqrt{3}}L'(p)-\frac{2}{3\sqrt{3}}L'(f_1)-\frac{1}{3\sqrt{3}}L'(f_2)\right)-\left(\frac{4}{3\sqrt{3}}L(p)-\frac{4}{3\sqrt{3}}L(f_1)\right),\\ \frac{1}{\sqrt{3}}\left(F'(s)+F'(d)+\frac{2}{9}F'(g)\right)&=\frac{1}{\sqrt{3}}\left(\frac{1}{\sqrt{3}}L'(p)-\frac{2}{3\sqrt{3}}L'(f_1)-\frac{1}{3\sqrt{3}}L'(f_1)\right)-\left(\frac{2}{3\sqrt{3}}L(p)-\frac{2}{3\sqrt{3}}L(f_1)\right).\end{aligned} \tag{23c}$$

The resulting determinant may be reduced to

$$\begin{vmatrix} \dfrac{F'(s)}{F(s)}+\dfrac{L'(f)}{L(f)} & \dfrac{1}{3}\left[\dfrac{F'(g)}{F(g)}+\dfrac{L'(f)}{L(f)}\right] & \dfrac{L'(f)}{L(f)}-\dfrac{L'(p)}{L(p)} \\ \dfrac{2L'(f)}{L(f)}-\dfrac{1}{3} & \dfrac{5}{18}\dfrac{L'(f)}{L(f)}+\dfrac{1}{9} & \dfrac{5}{2}\dfrac{L'(f)}{L(f)}-\dfrac{2}{3}+\dfrac{1}{\sqrt{3}}\dfrac{L'(p)}{L(p)}-\dfrac{L'(f)}{L(f)} \\ \dfrac{2F'(s)}{F(s)}+\dfrac{3F'(d)}{F(d)}-2 & \dfrac{4}{9}\dfrac{F'(g)}{F(g)}+2-\dfrac{F'(d)}{F(d)} & \dfrac{5F'(d)}{F(d)}-4 \end{vmatrix}. \tag{23d}$$

(b) F : Γ_2 odd ; Li : Γ_1 even.

The equations corresponding to this case may be derived from (a) by interchanging F and Li.

(c) F : Γ_3 odd ; Li : Γ_3 even.

In this case the odd functions selected were

$$p:\ x+y-2z,$$

$$f_1:\ x\left(x^2-\frac{3}{2}(y^2+z^2)\right)+y\left(y^2-\frac{3}{2}(x^2+z^2)\right)-2z\left(z^2-\frac{3}{2}(x^2+y^2)\right)$$

and the only even function was

$$d:\ x^2+y^2-2z^2.$$

(1) Continuity at (100) and (−100) for nearest neighbors in x direction

$$F(p)+F(f)=L(d),\quad F'(p)+F'(f)=L'(d). \tag{24}$$

(2) Continuity of z gradient at same point

$$-2F(p)+3F(f)=0. \tag{24a}$$

The secular equation yields

$$\frac{F'(p)}{F(p)}+\frac{5}{3}\frac{L'(d)}{L(d)}+\frac{2}{3}\frac{F'(f)}{F(f)}=0. \tag{24b}$$

V. (110) endpoint

The group R going with

$$k=\frac{3\pi}{4a}\begin{pmatrix}1\\1\\0\end{pmatrix}$$

is $C_2{}^v$ which has the character system

	E	C_2	C_v	$C_v{}^1$
Γ_1	1	1	1	1
Γ_2	1	1	−1	−1
Γ_3	1	−1	−1	1
Γ_4	1	−1	1	−1

where C_v and $C_v{}^1$ represent the two reflecting planes which pass through the (110) axis.

If we consider two neighbors in the x direction, the relative phases of Li and F, assuming the latter to be at the origin and the former at $-a$, is $e^{-i(3\pi/4)}$. The representatives of the group are the same for both polyhedra.

We may expect Γ_1 to go with the lowest surface again, while Γ_1, Γ_3, and Γ_4 go with the next band which is not degenerate at this point.

(a) Γ_1. The functions of type Γ_1 that were used are

$$s:\ 1,\quad p:\ x+y;\quad f:\ x^3+y^3-\frac{3}{2}(x+y)(xy+z^2).$$

(1) Continuity at (100) between nearest x neighbors

$$\begin{aligned} F(s)+i(F(p)+F(f))&=e^{i(3\pi/4)}[L(s)-i(L(p)+L(f))],\\ F'(s)+i(F'(p)+F'(f))&=-e^{i(3\pi/4)}[L'(s)-i(L'(p)+L'(f))]. \end{aligned}\tag{25}$$

(2) Continuity of y gradient at same point

$$F(p)-\frac{3}{2}F(f)=e^{i(3\pi/4)}\left(L(p)-\frac{3}{2}L(f)\right).\tag{25a}$$

These will furnish a point in both the first and the second band.

(b) Γ_3. The functions used in treating Γ_3 are

$$p:\ z,\quad d:\ z(x+y),\quad f:\ z\left(z^2-\frac{3}{2}(x^2+y^2)\right).$$

(1) Continuity at (001) and (00−1) for neighbors in z direction

$$F(p)+F(f_1)=-(L(p)+L(f)),\quad F'(p)+F'(f)=L'(p)+L'(f).\tag{26}$$

(2) Continuity of z gradient at (100) and (−100) for neighbors in x direction

$$\left[i\left(F(p)-\frac{3}{2}F(f)\right)-F(d)\right]=-\frac{1}{\surd 2}(1+i)\left[i\left(L(p)-\frac{3}{2}L(f)\right)+L(d)\right].\tag{26a}$$

(3) Continuity of neighbors in x direction at $(1/\surd 2\ 0\ 1/\surd 2)$ and $(-1/\surd 2\ 0\ 1/\surd 2)$.

$$\frac{1}{\surd 2}i\left[F(p)-\frac{1}{4}F(f)\right]-\frac{1}{2}F(d)=-\frac{1}{\surd 2}(1+i)\left[\frac{i}{\surd 2}\left(L(p)-\frac{L(f)}{4}\right)+\frac{1}{2}L(d)\right].\tag{26b}$$

(c) Γ_4. Functions employed:

$$p:\ (x-y),\quad d:\ z(x-y),\quad f_1:\ (x^3-y^3)-\frac{3}{2}(xy(x-y)+z^2(x-y),\quad f_2:\ x(y^2-z^2)-y(x^2-z^2).$$

(1) Continuity at $(1/\surd 2\ 0\ 1/\surd 2)$ and $(-1/\surd 2\ 0\ 1/\surd 2)$ for neighbors in x direction:

$$\left[i\left(\frac{F(p)}{\surd 2}-\frac{1}{4\surd 2}F(f_1)-\frac{1}{2\surd 2}F(f_2)\right)+\frac{1}{2}F(d)\right]=-e^{3\pi i/4}\left[i\left(\frac{1}{\surd 2}L(p)-\frac{1}{4\surd 2}L(f_1)=\frac{1}{2\surd 2}L(f_2)\right)+\frac{1}{2}L(d)\right].\tag{27}$$

(2) Continuity of x, y and z gradients at same point

$$\begin{aligned} &\frac{1}{\surd 2}\left[i\left(\frac{F'(p)}{\surd 2}-\frac{1}{4\surd 2}F'(f_1)-\frac{1}{2\surd 2}F'(f_2)\right)+\frac{F'(d)}{2}\right]+\frac{1}{2}\left[i\left(\frac{F'(p)}{\surd 2}+\frac{9}{4\surd 2}F(f_1)+\frac{1}{2\surd 2}F(f_2)\right)\right.\\ &\qquad=e^{(3\pi/4)i}\left[\frac{1}{\surd 2}\left\{i\left(-\frac{L'(p)}{\surd 2}+\frac{1}{4\surd 2}L'(f_1)+\frac{1}{2\surd 2}L'(f_2)\right)-\frac{L'(d)}{2}\right\}\right.\\ &\qquad\qquad\left.+\frac{1}{2}\left\{i\left(\frac{L(p)}{\surd 2}+\frac{9}{4\surd 2}L(f_1)+\frac{1}{2\surd 2}L(f_2)\right)\right\}\right], \end{aligned}\tag{27a}$$

$$i\frac{1}{\sqrt{2}}F(p)+\frac{1}{2}F(d)=e^{(3\pi/4)i}\left(i\frac{L(p)}{\sqrt{2}}+\frac{L(d)}{2}\right), \tag{27b}$$

$$\frac{1}{\sqrt{2}}\left[i\left(\frac{F'(p)}{\sqrt{2}}-\frac{1}{4\sqrt{2}}F'(f_1)-\frac{1}{2\sqrt{2}}F'(f_2)\right)+\frac{F'(d)}{2}\right]-\frac{1}{2}i\left(\frac{F(p)}{\sqrt{2}}-\frac{9}{4\sqrt{2}}F(f_1)+\frac{1}{2\sqrt{2}}F(f_2)\right)$$
$$=e^{(3\pi/4)i}\left[\frac{1}{\sqrt{2}}\left\{i\left(\frac{-L'(p)}{\sqrt{2}}+\frac{L'(f_1)}{4\sqrt{2}}+\frac{L'(f_2)}{2\sqrt{2}}\right)-\frac{L'(d)}{2}\right\}+\frac{1}{2}i\left(\frac{L(p)}{\sqrt{2}}+\frac{9}{4\sqrt{2}}L(f_1)+\frac{L(f_2)}{2\sqrt{2}}\right)\right]. \tag{28}$$

PART B. APPLICATION TO LiF AND LiH

4. The self-consistent field

In order to obtain the Hartree self-consistent field for the system of filled bands, it would be necessary to obtain the charge distribution arising from all electrons by summing $|\psi_k|^2$ over all bands at each step of the conventional Hartree procedure. Instead of doing this, we have taken the set of eight wave functions for $k=0$ going with the two filled bands of LiF, normalized each of these to 1 within the unit cell and used the spherically symmetric part of the sum of $|\psi_k|^2$ for these as the charge distribution within each of the polyhedra in terms of which the field is computed. In the case of LiH, the two states for $k=0$ going with the single filled band were used. This procedure seems entirely justifiable for the present purposes since the work on monovalent metals shows that the function going with $k=0$ always gives a good representation of the charge distribution and the same may be expected here.

Using this scheme, we have obtained a self-consistent charge distribution for the lattice, treating eight valence electrons in the case of LiF and two in that of LiH. We employed Hartree's potential for the $(1s)^2$ configuration of F^-,[13] the ion core field for Li^+ developed by one of us,[14] and, of course, the Coulomb field for H. We first selected what seemed to be a reasonable charge distribution for the valence electrons, basing our judgment upon the atomic wave functions, and then computed an effective potential for this distribution. This was added to the ion core field and the potential to obtain the potential field within each of the polyhedra arising from the enclosed charge. The spherically symmetric part of the Madelung potential from all of the external ions was added to the field within a given polyhedron in the cases in which the polyhedra were not electrostatically neutral, in order to obtain the total field. Using this and the results of Section 3, the wave functions going with $k=0$ were computed and a new charge distribution was obtained. This was then compared with the previously assumed one and a new choice of

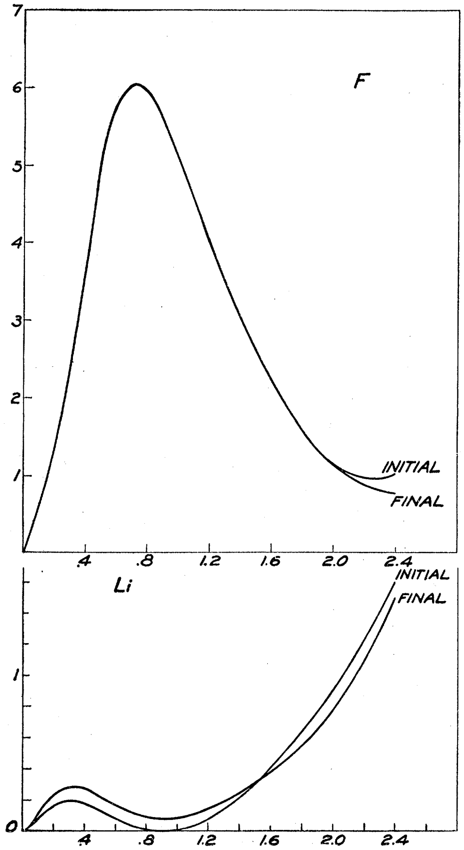

FIG. 1. The initial and final radial charge distributions for F and Li in LiF are plotted on a relative scale of ordinates. The abscissas are in Bohr units and the critical radius r_s of 2.4 corresponds to the radius of the s sphere that was used. These results are valid for the Hartree, not the final, approximation.

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[13] D. Hartree, Proc. Roy, Soc. **A151**, 96 (1935).

[14] F. Seitz, Phys. Rev. **47**, 400 (1935).

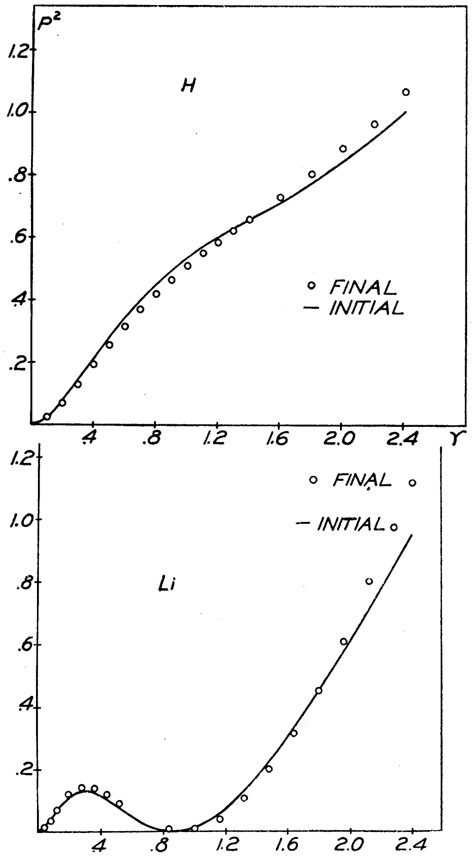

FIG. 2. Same as Fig. 2 for LiH.

starting field was made on the basis of the agreement.

The procedure is actually rather a tedious one to carry through, mainly because one may not use some simple mean between the initial and final charge distribution of one trial in order to obtain a good starting distribution for the next. This lack of stability arises from the fact that wave functions in neighboring cells do not affect one another only because of their potential interaction, but also because of the continuity conditions which they must satisy.

The charge distributions, from the "s sphere approximation" standpoint, which lead to a practically self-consistent solution are shown in Figs. 1 and 2 for LiF and LiH, respectively. In the first case, the initial distribution was taken to be of such a type that the Li and F spheres were electrostatically neutral, and the final distribution was such as to give the F sphere a charge of $-0.2e$ and the Li sphere the negative of this. Actually the self-consistent solution is much nearer the starting one, and were the normalization carried through in such a way that the total charge on the F sphere were $-0.05e$ and that on the Li $+0.05e$, the field would be self-consistent. We have used the starting field going with this case in the following because the neglect of exchange in the computations is greater than the error made in not using the exact Hartree self-consistent field. The case of LiH is much easier to handle because the situation is inherently simpler, and in this case the initial and final distributions form a self-consistent solution in which the H has an excess of 0.35 electron and the Li a deficit of the same amount.

The total potential in each of the spheres is shown in Fig. 3 for LiF. The way in which these have been joined at $r=2.4a_h$ is a consequence of the s sphere approximation and has no significance other than that it shows, roughly, how the potential varies in going from one ion to its nearest unlike neighbor.

The neglect of the Fock terms in the self-consistent equations is, without question, not quantitatively justifiable. Nevertheless, it may be made clear that these will not lead to a justification of the classical concepts by use of the following arguments.

In the first place, the classical picture would be valid only if there were a self-consistent solution of the Heitler-London type in which the

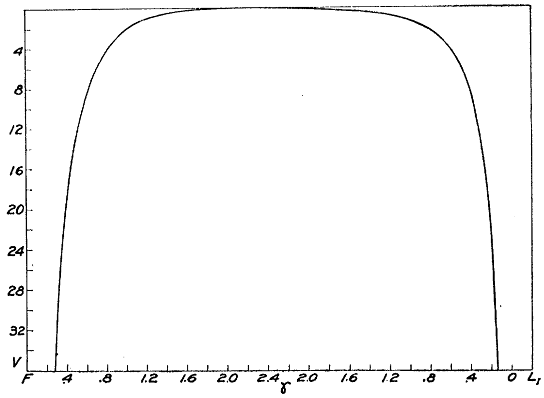

FIG. 3. The Hartree potential in LiF is schematically represented. The ordinates are in Rydberg units and the abscissas in Bohr radii. The junction at 2.4 is connected with the use of the spherical approximation so that the illustrated internuclear distance is not the observed one. Actually the (100) distance is less than this by a factor of 2/2.4.

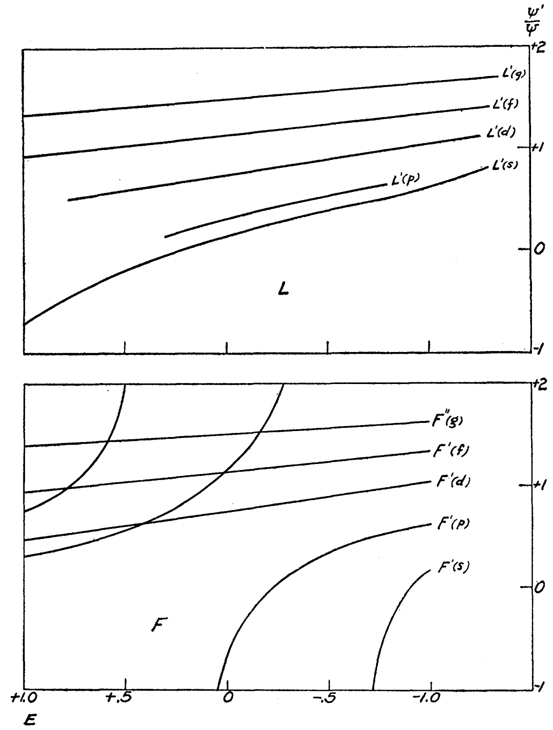

FIG. 4. The ratios x'/x (i.e., L' and F') for the radial functions of interest at the point $r_s=2.4a_0$ are plotted as a function of the energy, in Rydberg units.

valence electron wave functions used are localized about the F (we shall use the case of LiF as an example), and have zero amplitude wherever the Li field is appreciable (e.g. within our Li sphere). This is clearly not possible since the F^- solution of Hartree has a charge of 0.9 outside of our s sphere. This charge is in the region of the Li fields and will distribute itself symmetrically about the Li nuclei. We may expect the charge distribution to be pulled toward the F atoms when one uses Fock's equations, but this will not lead to completely ionized Li since the Fock and Hartree fields for the Na^+ are very similar.[15] Correlation effects will change this by only a small amount if the case of He may be used as an example. We estimate that the negative charge excess of the F sphere, over a neutral value, will lie between 0.25 and 0.5 electron. In the case of LiH, exchange and correlation effects will not be nearly as important since there are fewer electrons, and an examination of the H^- solution of Bethe shows clearly that the Li atom cannot be completely ionized in this case either. That is, Heitler-London functions which are centered about H and have zero amplitude on the Li region will not form a self-consistent solution.

Since the Madelung-Born computations for both LiF and LiH agree very closely with the experimental values,[16] and the present work shows that the necessary conditions for the justification of the ionic crystal model are not met with, we are inclined to the belief that the agreement of the former is purely fortuitous and that a large part of the heat of sublimation of ionic crystals arises from the same source as the binding energies of metals and valence crystals. That is, the binding energies are not primarily connected with the fact that the Li ion is left in a region where no valence electrons reside; but is mainly dependent upon the fact that the electrons in a crystal may be at regions of favorable potential (the Li and F nuclei, etc.) in a correlated way. This does not mean that the electrostatic field of the Li ion does not play an extremely important role, but rather that the change in the electronic wave functions in going from the gaseous to the solid state plays at least as important a role. We hope to verify this aspect of the situation more completely by a quantitative computation on LiH, which is the most ideally suited substance. In order to do this, it is absolutely essential to take into account exchange and correlation effects since these are of the same order of magnitude as the heat of sublimation in this case, just as in that of metals.[17]

5. The distribution of energy bands

A. LiF

Using the equations of Section 3, we have determined the energy bands of both LiF and LiH with the field corresponding to the Hartree approximation. The ratios ψ'/ψ at $r_s=2.4a_h$ as a function of energy for each of the important

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[15] V. Fock and M. Petraschen, Physik. Zeits. Sowjetunion **6**, 368 (1934). See also Hartree, Proc. Roy. Soc. **A150**, 9 (1935) for case of Be.

[16] J. Sherman, Chem. Rev. **11**, 93 (1932).

[17] The Hartree solution for Cl^- (Proc. Roy. Soc. **A141**, 282 (1933)) shows that these remarks will be just as true for the alkali chlorine compounds as for the fluorides. About 1.5 electrons lie byeond the radius corresponding to half the minimum distance in NaCl, for example, and, as a result, overlap into the closed shell region of the Na ions.

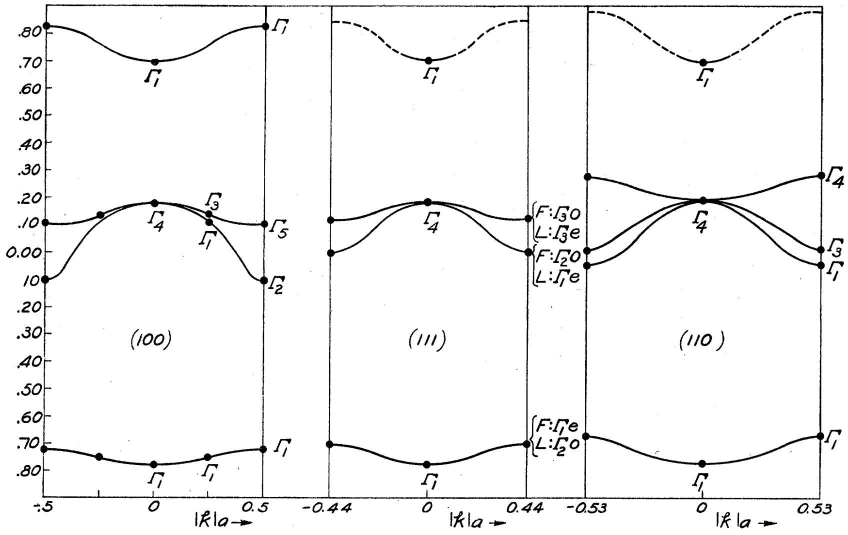

FIG. 5. $E(k)$ plots for three prominent crystallographic directions. The ordinates are Rydberg units. It is to be emphasized that these results are only approximate.

radial functions are shown in Fig. 4. This choice of the radius of the s sphere is valid in both LiF and LiH. It is to be emphasized that only the relative positions of the bands in a given solid have significance because of the neglection of exchange and correlation effects.

The energies going with the various wave functions are tabulated in Table I for LiF, and the probable positions of the bands are shown in Fig. 5. The wave functions for $k=0$ going with the first three bands are shown in Fig. 6. These have been joined at r_s instead of the actual midway point, in accordance with the s sphere approximation, but the general form is representative. The difference in energy between center points of the second (filled band) and the upper band correspond to the long wave-length limit of the absorption band of LiF and is found here to be about 1500A, as compared[18] with the observed value of about 1200. We would naturally expect to get too low a value for the energy difference since exchange effects are more important for electrons of the same type as those giving rise to the field than for others, as Bardeen[19] has shown, so that the lowest band will be pushed down more than the upper, unfilled band.

TABLE I. *E(k) for particular points in LiF.*

Band	I	II	III	IV	V
$k=0$	−0.77	+0.18	0.18	0.18	0.7
(100) Limit	−0.73	0.10	0.10	−0.11	0.82
(100) Midpoint	−0.75	0.15	0.15	0.12	
(111) Limit	−0.76	0.12	0.12	0.03	
(110) Limit	−0.68	0.01	0.05	0.07	

It is to be observed that the wave function going with the unfilled band is much more like that for a free electron than are the other functions.

B. LiH

The ψ'/ψ ratios for LiH are shown in Fig. 7 and the positions of the bands for the (100) direction of propagation is shown in Fig. 8. Only the lowest band is filled in this case, and the wave function going with $k=0$ is illustrated in Fig. 9. The energy difference of the end points of the first and second bands corresponds to an absorption wave-length of 1900A which is in agreement with the value of 1900A found by Bach and Bonhoeffer.[20] The accuracy of agreement is, of course, not particularly significant and, as a matter of fact, these workers observe

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[18] F. H. Melvin, Phys. Rev. **37**, 1230 (1931); E. G. Schneider, Phys. Rev. **49**, 341 (1936).

[19] J. Bardeen, Phys. Rev. **49**, 653 (1936).

[20] F. Bach and K. F. Bonhoeffer, Zeits. f. physik. Chemie **23**, 256 (1933). In connection with the remarks made in the text, it is worth emphasizing the fact that a stoichemical excess of one substance in a compound (or an impurity) will give rise to localized electronic states which lie between the bands. These will undoubtedly possess sharper absorption peaks than the band to band transitions do.

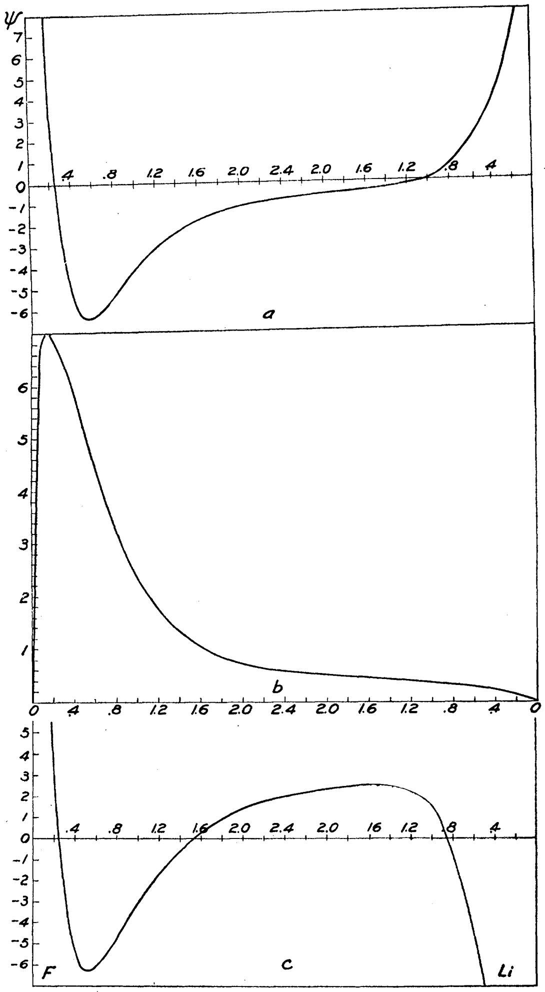

FIG. 6. Relative scale plots of the three prominent wave functions for $k=0$. a and b go with the first and second filled hand and c goes with the first unfilled one.

another absorption peak at 2500A. This is so narrow that it seems improbable that it is connected with a volume effect, but more likely that it is either a surface absorption of the same type met with in photoelectric effect, or is connected with the presence of an excess of Li. For this reason we feel inclined to make the present assignment. As we have stated above, we are in the process of extending this work on LiH in order to obtain more quantitative results.

6. Critique of viewpoint

In cases such as the present one in which F^- and Li^+ form closed shell configurations, it is always preferable to use Bloch type of eigenfunctions rather than a Heitler-London scheme in which the valence electrons are viewed as being centered about one type of atom (F), but to extend into the region of the other (Li), at least as long as aperiodic phenomena are not considered. This is true since one can always take an appropriate linear combination of the rows or columns of given spin in the total determinantal eigenfunction, if Heitler-London functions are used, in such a way as to obtain a new determinant in which the elements are of Bloch form. A suitable linear combination of atomic orbitals would be

$$\psi_k=\sum_\alpha e^{ik\cdot r_\alpha}\Big(\sum_i a_i\psi(r_\alpha,\,i)\Big) \qquad (29)$$

where ψ_k is the Bloch eigenfunction, $\psi(r_\alpha, i)$ is the Heitler-London function for the electron centered about the ith atom of the αth unit cell, and the a's are constants. In the case of LiF, for example, the ψ's might appropriately be centered about the F atom, though they would extend into the Li region. Since the best Bloch function which would satisfy Fock's equation, would generally be different from (29) (except for the case of x-ray electrons in which case they would be the same), they would yield a better binding energy than the Heitler-London scheme would. For this reason the use of Bloch eigenfunctions is

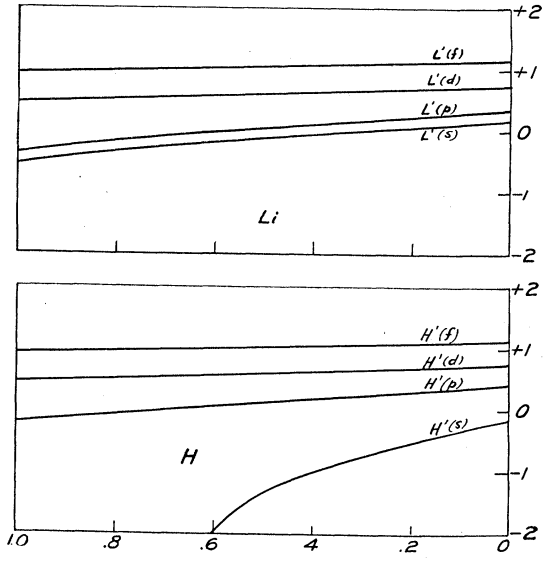

FIG. 7. Same as Fig. 4, but for LiH.

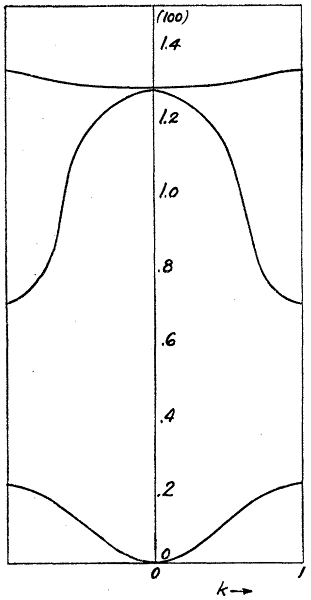

FIG. 8. Same as Fig. 5, but for LiH.

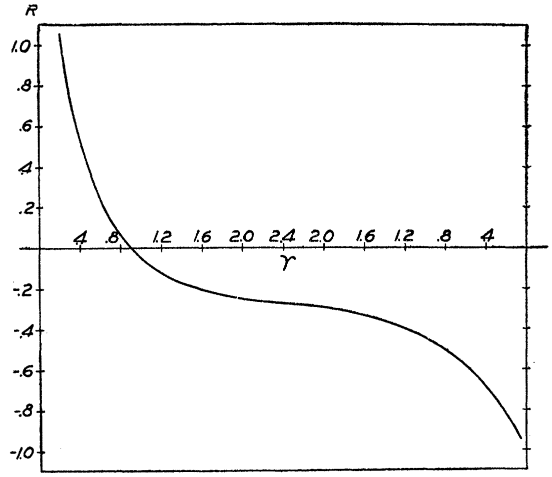

FIG. 9. Same as Fig. 6, but for LiH.

justifiable as long as it is implied that there are correlational modifications.[21]

One now approaches the question of whether one should use Heitler-London or Bloch eigenfunctions in the description of a situation in which one electron is in an excited state and the filled band is left with a dearth of one electron (as usual we shall refer to this as an anti-electron). In the case of both LiF and LiH it seems unquestionable that one should use the Bloch functions for the excited electron since these functions are essentially those of free electrons and differ markedly from the states of the filled band. Even in the case of the anti-electron, however, we believe that it is more appropriate to consider a Bloch rather than a Heitler-London eigenfunction to be absent, simply because the energy of these electrons is such that the electron may jump from one atom to the next with ease. That is, there is no question of a very small probability of leakage through a barrier as in the case of x-ray electrons, simply because the wave function has an appreciable amplitude at all points. It is probably true, however, that the anti-electron is conducted through the lattice at a much slower rate than the electron in the excited state.

On the other hand, there are unquestionably states in which the electron is strictly localized to a definite position such as those corresponding to the U centers in ionic crystals or to surface states. When an electron makes a transition from such a state to a free state, the anti-electron created may very well be localized in certain cases. For example, if the U center arises from an electron bound to an excess Li ion which is an open space in the lattice, the locality of this ion may remain positively charged when the electron is removed by light absorption, simply because the other electron present which will be in the upper filled band will not be able to extend over the open space sufficiently well to completely neutralize it. That is, one may regard the situation as if a Li ion were attached to the "surface" of a hole. We do not feel justified in entering into more speculations of this type in the present paper, though it is felt that the viewpoint emphasized here is capable of explaining most of the conduction properties of halide crystals, and intend to return to this on another occasion.

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[21] In a recent paper (Physik. Zeits. Sowjetunion **9**, 158 (1936)) Frenkel attempts a criticism of the use of the Bloch picture in such cases as the present one. We believe that this criticism is not justifiable to the extent this author presses it for the reasons mentioned here.