

POSITRONIUM IN LITHIUM FLUORIDE

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Dedicated to my beloved Josephine

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## ABSTRACT

The possibility that positronium can form and persist in ionic crystals was a matter of doubt until Neamtan and Verrall<sup>R(1)</sup> did a quantitative investigation in the lithium hydride crystal and found that an Ore gap exists for such a crystal. Following in part a similar procedure the present work examines the possibility for the case of lithium fluoride.

The crystal potential is approximated by means of a sum of central field potentials centred on the ion sites. The potential due to a lithium ion is taken from R(1). The potential due to a fluorine ion obtained by a self-consistent field method is fitted to a Coulomb-plus-Yukawa form. Then perturbation theory is applied to provide a wavefunction to give an upper bound for the ground state energy of positronium in the crystal.

The electron energy gap at the boundary of the first Brillouin zone is estimated by a variational method. The trial wavefunctions used for variation are obtained by an examination of the crystal space group and its symmetry properties.

Similarly, the ground state energy of a positron in the crystal is obtained by choosing a trial wavefunction having

maximum symmetry of the crystal space group.

The ground state energy of positronium in the crystal is found to be -17.54 e.v.; the electron energies at the top of the valence band and at the bottom of the conduction band are found to be -17.03 e.v. and -8.14 e.v. respectively, giving an energy gap of 8.89 e.v.. The ground state energy of a positron in the crystal is found to be -3.99 e.v., polarization effects due to the positron being neglected.

With these results, energetic considerations show that there is an Ore gap for positronium formation and persistence in the crystal provided polarization effects are much less than 5 e.v., which is likely the case.

## CHAPTER ONE

### INTRODUCTION

A positron can annihilate with an electron in the following manners:

- (1) It can collide and annihilate with an electron in flight.
- (2) It can form a hydrogen-like system, called 'positronium' with an electron in the singlet state and then annihilate with a mean life of  $1.25 \times 10^{-10}$  sec..

(1) and (2) are ordinarily not experimentally resolved. They are often referred to as the  $\tau_1$  component, with a mean life of the order of  $10^{-10}$  sec., which varies from substance to substance, and they are both two-photon annihilation processes

- (3) It can form positronium with an electron in the triplet state and then annihilate with a mean life of  $1.4 \times 10^{-7}$  sec., emitting three photons.

There is a relatively longer component than the  $\tau_1$ , called the  $\tau_2$  component, with a mean life of the order of  $10^{-9}$  sec., also emitting two photons, which according to Wallace<sup>R(2)</sup> can be explained by

- (4) the 'Pickoff' decay, in which the positron forms positronium with an electron in the triplet state and then the positron annihilates not with the bound electron but with another free electron in the singlet state, thus emitting two photons, and owing to the screening effect of the bound electron, the annihilation

lation mean life will be longer.

If the 'Pickoff' theory is correct, then one should expect that in substances where  $\tau_2$  components are discovered a positron with energy falling within a certain range will be able to form positronium with an electron and vice versa. This allowable energy range is called an Ore gap. Ferrell<sup>R(3)</sup> once pointed out that from a qualitative point of view it is rather unlikely that positronium can form and persist in ionic crystals. Neamtan and Verrall<sup>R(1)</sup>, however, did a quantitative investigation and found that energetic considerations favour the existence of an Ore gap for positronium formation and persistence in a lithium hydride crystal. Meanwhile  $\tau_2$  components in positron annihilation have been reported in a number of ionic crystals<sup>R(4)</sup>, chiefly alkali halides, and including lithium hydride. The present work is to study such a possibility in a lithium fluoride crystal.

In this thesis, atomic units will be used consistently throughout unless otherwise specified. The electronic charge  $e$  will be taken to be unity. Lengths will be expressed in units of  $a_0$ , the first Bohr radius, and energy will be expressed in units of  $e^2/a_0$ .

References and appendices will be denoted and ordered as R(1), R(2), R(3)...; A(1), A(2), A(3)...etc. respectively.



## CHAPTER TWO

### THE CRYSTAL POTENTIAL OF LITHIUM FLUORIDE

The crystal of lithium fluoride is of face-centred-cubic structure, the positive lithium ion being relatively small and the negative fluorine ion quite extended. The crystal potential, as an approximation, is taken to be a simple sum of contributions from individual free ions located at the ion sites, the deformation of these ions due to their presence in the crystal being for our present purpose neglected. Thus we would like to find first the potentials due to a positive and a negative ion respectively. The potential due to each such ion can be adequately approximated by a Coulomb-plus-Yukawa form.

The potential due to a lithium ion at a distance  $R$  is, according to R(1), given by

$$v_1(\underline{R}) = \frac{1}{R} + \frac{2}{R} e^{-\alpha R} \quad (2-1)$$

where  $\alpha = 2.20$  in units of  $a_0^{-1}$ .

The fluorine ion consists of a nucleus of charge 9 with 10 orbital electrons. Since the 1S and 2S electrons are bound closer to the nucleus, as an approximation, we can regard them as forming an entity with the nucleus. Hence the ion will be treated as consisting of a nucleus of charge 5 plus 6 valency electrons. These 6 electrons

are naturally the  $2p_x$ ,  $2p_y$ , and  $2p_z$  electrons. Their wavefunctions are taken to be of the following forms:

$$\begin{aligned}\psi_x &= KP(R) \sin\theta \sin\phi \\ \psi_y &= KP(R) \sin\theta \cos\phi \\ \psi_z &= KP(R) \cos\theta\end{aligned}\tag{2-2}$$

where  $K$  is a constant to be determined by normalization,  $P(R)$  is the radial wavefunction, a variable whose form is to be chosen,

$\theta$  and  $\phi$  are polar angles.

Reference is now made to the article: "Quantum mechanical treatment of lithium fluoride"<sup>R(5)</sup>, in which the radial wavefunction  $P(R)$  is chosen as

$$P(R) = R(A_1 e^{-\alpha_1 R} + A_2 e^{-\alpha_2 R})\tag{2-3}$$

where  $A_1$ ,  $A_2$ ,  $\alpha_1$ ,  $\alpha_2$  are parameters to be determined by the self-consistent field method of Hartree.

In the reference quoted, their values were obtained as follows:

$$A_1 = 7.23$$

$$A_2 = 0.31$$

$$\alpha_1 = 2.37 a_0^{-1}$$

$$\alpha_2 = 0.85 a_0^{-1}$$

Now the interaction energy of an electron at a distance  $r$  from a fluorine ion site is given by

$$-\frac{5}{r} + \Delta w(r) \tag{2-4}$$

The first term in the above expression is the interaction energy with the effective nucleus; the second term represents that with the 6 valency electrons which are distributed in space, with probability distribution  $|\psi_x|^2 d\tau$ ,  $|\psi_y|^2 d\tau$ ,  $|\psi_z|^2 d\tau$  etc. in an elementary volume, or rather, with charge distribution  $-2|\psi_x|^2 d$ , etc., there being two electrons of opposite spin in each such state.

Let the test electron be at a distance  $r$  from the nucleus, a distance  $r'$  from the elementary volume  $d$ , which in turn is at a distance  $R$  from the nucleus, as shown in fig. 1.

Then,

$$\begin{aligned} \Delta w(r) &= 2 \left[ \int \frac{|\psi_x|^2 d\tau}{r'} + \int \frac{|\psi_y|^2 d\tau}{r'} + \int \frac{|\psi_z|^2 d\tau}{r'} \right] \\ &= 2 \int \frac{K^2 P(R)^2}{r'} d\tau \end{aligned} \tag{2-5}$$

where for normalization,  $K = (3/4\pi)^{\frac{1}{2}}$

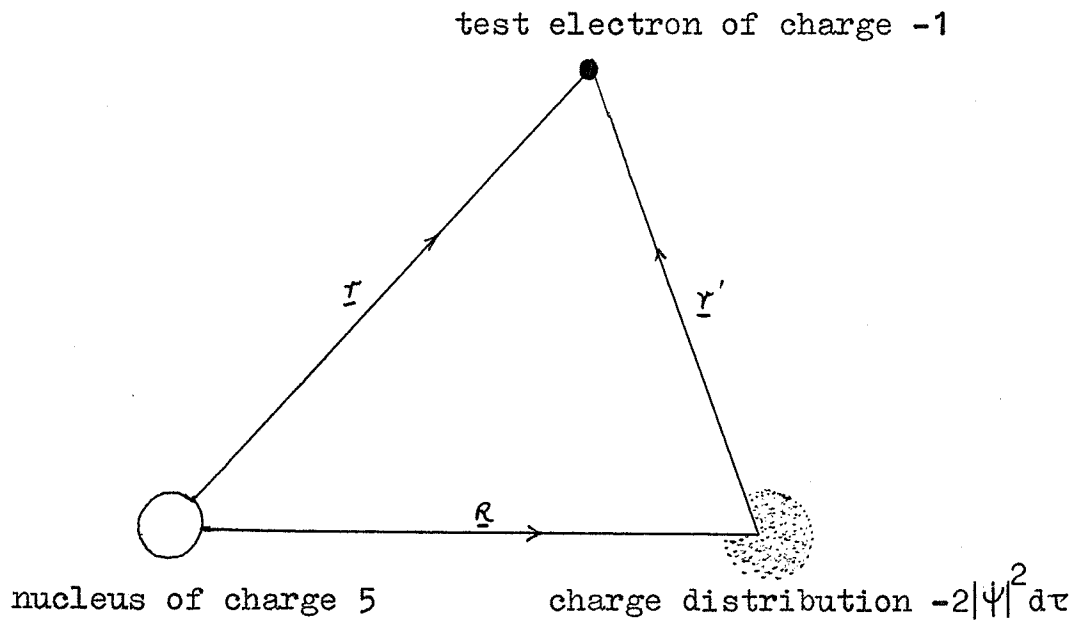


fig. 1

Now we would like to obtain an expression for  $d\tau$  in terms of the variables  $R$ ,  $r'$  and  $\alpha$ , which is the angle of rotation of the plane formed by  $\underline{r}'$  and  $\underline{R}$  about the axis  $\underline{r}$ . It can be shown ( see A(1) ) that

$$d\tau = \frac{r'R}{r} dr' dR d\alpha \quad (2-6)$$

Since the integrand in (2-5) does not depend on  $\alpha$ , we have

$$d\tau = \frac{2\pi}{r} R r' dR dr'$$

Therefore (2-5) becomes

$$\Delta w(r) = 2K^2 \int_0^R \frac{(A_1^2 e^{-2\alpha_1 R} + A_2^2 e^{-2\alpha_2 R} + 2A_1 A_2 e^{-(\alpha_1 + \alpha_2)R})}{r'} 2\pi R r' dr'$$

$$= \left[ - \sum_{i=1}^2 \sum_{j=1}^2 \frac{6A_i A_j}{(\alpha_i + \alpha_j)^2} e^{-(\alpha_i + \alpha_j)r} \left( r^2 + \frac{6r}{(\alpha_i + \alpha_j)} + \frac{18}{(\alpha_i + \alpha_j)^2} + \frac{24}{(\alpha_i + \alpha_j)^3 r} \right) \right] + \frac{6}{r}$$

∴ (2-4) becomes

$$\left[ - \sum_{i=1}^2 \sum_{j=1}^2 \frac{6A_i A_j}{(\alpha_i + \alpha_j)^2} e^{-(\alpha_i + \alpha_j)r} \left( r^2 + \frac{6r}{(\alpha_i + \alpha_j)} + \frac{18}{(\alpha_i + \alpha_j)^2} + \frac{24}{(\alpha_i + \alpha_j)^3 r} \right) \right] + \frac{1}{r}$$

Hence the potential at a distance  $r$  due to a fluorine ion is given by

$$v_2(r) = \left[ \sum_{i=1}^2 \sum_{j=1}^2 \frac{6A_i A_j}{(\alpha_i + \alpha_j)^2} e^{-(\alpha_i + \alpha_j)r} \left( r^2 + \frac{6r}{(\alpha_i + \alpha_j)} + \frac{18}{(\alpha_i + \alpha_j)^2} + \frac{24}{(\alpha_i + \alpha_j)^3 r} \right) \right] - \frac{1}{r} \quad (2-7)$$

(2-7) is a spherically symmetric potential. We can fit it to a Coulomb-plus-Yukawa form. We write

$$v_2(r) = - \frac{1}{r} + c \frac{e^{-\beta r}}{r} \quad (2-8)$$

which has the requisite behaviour for small  $r$  and large  $r$ .

(2-8) then is equated to (2-7), and  $\beta$ ,  $c$  are determined by a

graphical method.

Let  $Y$  be the terms in (2-7) other than the Coulomb term.

Write 
$$Y = \frac{ce^{-\beta r}}{r}$$

$$\therefore \log(rY) = \log c - \beta r \quad (2-9)$$

It can be seen from the graph<sup>p.13</sup> that we cannot fit an exact straight line. However, since the crystal parameter is about  $4a_0$ , we would like to have a good fit over the region  $1 < r < 4$ , because an electron is unlikely to be too close to the origin, or to a positive ion. So we require our straight line to be the tangent to the curve in the region  $1 < r < 4$ .

From the graph, the slope = 1.27

the intercept = 1.55

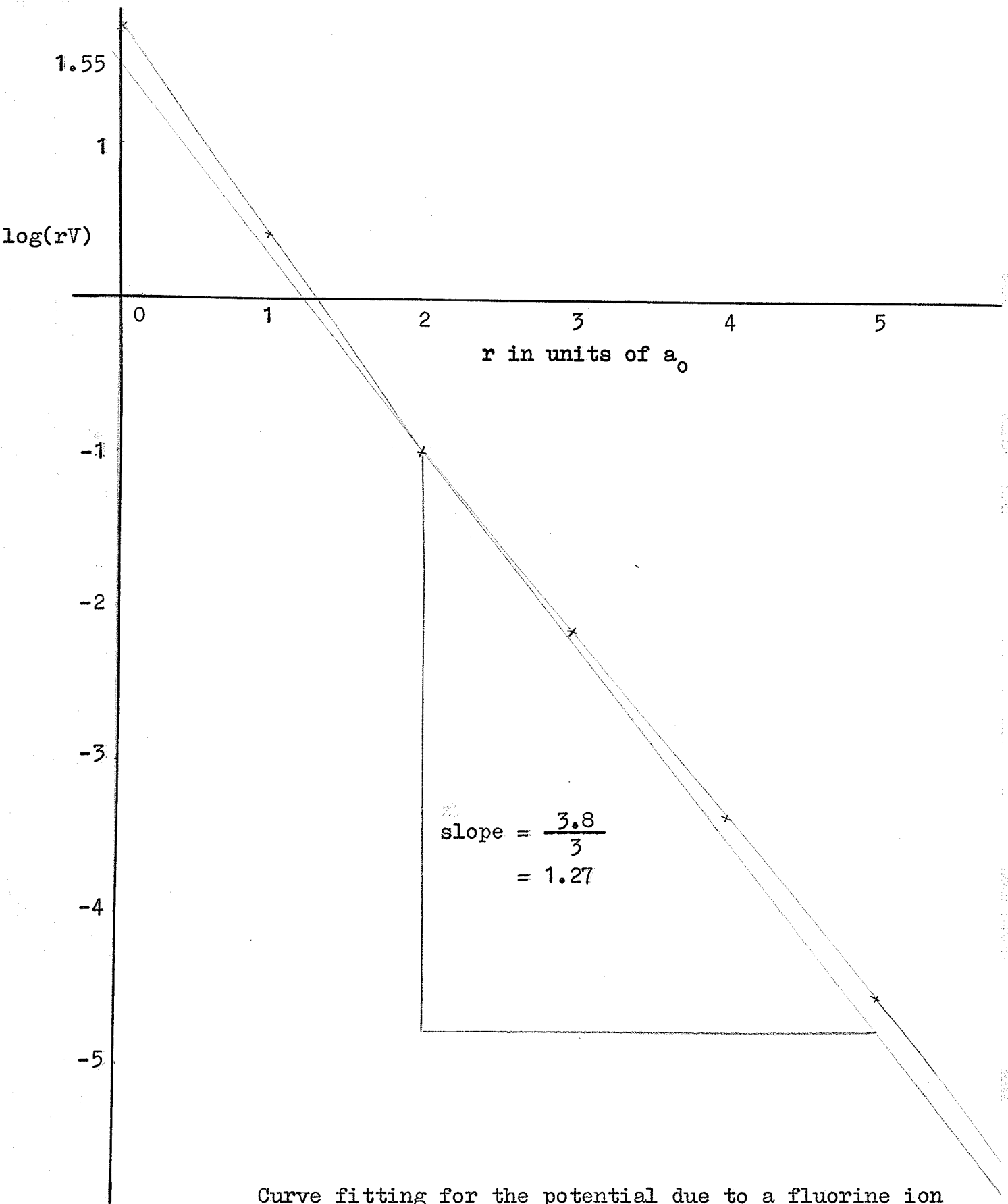
$$\therefore \beta = 1.27 a_0^{-1} \quad (2-10)$$
$$c = 4.70$$

The lithium fluoride crystal potential then is given by

$$V(\underline{R}) = \sum_j \left[ v_1(\underline{R}-\underline{R}_j) + v_2(\underline{R}-\underline{R}_j-\underline{a}) \right] \quad (2-11)$$

where  $\underline{R}_j$  is the position vector of the  $j$ th. positive ion

and  $\underline{a}$  is the position vector of a negative ion with respect to an origin at the location of a positive ion.



Curve fitting for the potential due to a fluorine ion



### Fourier analysis of the crystal potential

Since  $V(\underline{R})$ , the crystal potential, has the periodicity of the lattice, we can expand it as a Fourier series.

$$\therefore V(\underline{R}) = \sum_{\underline{K}} C_{\underline{K}} e^{2\pi i \underline{K} \cdot \underline{R}} \quad (2-12)$$

where  $\underline{K}$  is a vector of the reciprocal lattice.

$$C_{\underline{K}} = \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\tau_R} e^{-2\pi i \underline{K} \cdot \underline{R}} V(\underline{R}) d\tau_R \quad (2-13)$$

where  $\tau_R$  is a box of side  $S$ .

It can be shown ( see A(2) ) that

$$\begin{aligned} C_{\underline{K}} &= C_{-\underline{K}} = C_{n_1 n_2 n_3} \\ &= \frac{2\pi}{L^3} \left[ \frac{2}{k^2 + \alpha^2} + \frac{1}{k^2} + (-1)^{n_1 + n_2 + n_3} \left( \frac{4.7}{k^2 + \beta^2} - \frac{1}{k^2} \right) \right] \end{aligned} \quad (2-14)$$

$$\text{where } k^2 = \frac{\pi^2}{L^2} \left[ (n_2 + n_3 - n_1)^2 + (n_3 + n_1 - n_2)^2 + (n_1 + n_2 - n_3)^2 \right] \quad (2-15)$$

and  $L = 3.78 a_0^{R(5)}$  is the crystal parameter.

In the above,  $C_{\underline{K}}$  is expressed in units of  $e/a_0$ .

### CHAPTER THREE

#### THE GROUND STATE ENERGY OF POSITRONIUM IN THE CRYSTAL

The methods, mathematical equations and expressions involved here in this chapter will be very much similar to those in Verrall's thesis<sup>R(1)</sup>. That is, the crystal potential is considered as a perturbation to the free positronium. Owing to parity considerations, the first order energy shift, as well as all odd orders, vanishes. So second order approximation will be good to third order. The second-order corrected wavefunction will be used to give an upper bound to the ground state energy of positronium in the crystal.

The total Hamiltonian of positronium moving in the crystal is

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{|\underline{r}_2 - \underline{r}_1|} + V(\underline{r}_1) - V(\underline{r}_2) \quad (3-1)$$

where the subscripts 1 and 2 denote the positron and the electron respectively.

Working in centre-of-mass coordinates and relative coordinates, we have

$$H = -\frac{1}{4}\nabla_R^2 - \nabla_r^2 - \frac{1}{r} + V(\underline{R} - \frac{\underline{r}}{2}) - V(\underline{R} + \frac{\underline{r}}{2}) \quad (3-2)$$

where

$$\underline{R} = \frac{1}{2}(\underline{r}_1 + \underline{r}_2), \quad \underline{r} = \underline{r}_2 - \underline{r}_1$$

$$\text{Write } H = H_0 + H_1 \quad (3-3)$$

where  $H_0 = -\frac{1}{4}\nabla_R^2 - \nabla_r^2 - \frac{1}{r}$  is the unperturbed Hamiltonian,

$H_1 = V(\underline{R}-\frac{\underline{r}}{2}) - V(\underline{R}+\frac{\underline{r}}{2})$  is the perturbing

term.

The eigenfunctions of  $H_0$  are

$$\psi_{\underline{k},nlm} = e^{i\underline{k}\cdot\underline{r}} \phi_{nlm}(\underline{r}) \quad (3-4)$$

with eigenvalue  $E_n + \frac{1}{4}k^2$

where  $E_n = \frac{1}{2} \times$  the excited nth level of the hydrogen atom.

The second-order wavefunction that we shall need for giving an upper bound to the ground state energy of positronium in the crystal is given by

$$\psi = \psi_{0,100} + \sum_{\substack{\underline{k},nlm \\ \underline{k} \neq 0}} \frac{(\psi_{0,100} | H_1 | \psi_{\underline{k},nlm})}{(E_1 - E_n - \frac{1}{4}k^2)} \psi_{\underline{k},nlm} \quad (3-5)$$

The upper bound is given by

$$\mathcal{E} = \frac{(\psi | H | \psi)}{(\psi | \psi)} \quad (3-6)$$

For detail of evaluation of  $(\psi | H | \psi)$  and  $(\psi | \psi)$ , see Verrall's thesis<sup>R(1)</sup> and also A(3). The relevant expressions and equations in R(1) have been checked to be correct except the expression for  $(\psi | H | \psi)$ , which will be quoted below in its

corrected form.

$$\begin{aligned}
 (\psi|\psi) &= 1 + 2 \sum_{\underline{K}} \frac{|c_{\underline{K}}|^2 \left(1 - \frac{1}{(1+k^2)^2}\right)}{(E_1 - \frac{1}{4}k^2)^2} \\
 &\quad + 16\pi \sum_{\underline{K}} \sum_{n=2}^5 \sum_{\text{odd } l} |c_{\underline{K}}|^2 (2l+1) (I_{n,1})^2 \left[ \frac{1}{(E_1 - E_n - \frac{1}{4}k^2)^2} - \frac{1}{(E_1 - \frac{1}{4}k^2)^2} \right]
 \end{aligned} \tag{3-7}$$

$$\begin{aligned}
 (\psi|H|\psi) &= E_1 + 2 \left\{ 2 \sum_{\underline{K}} \frac{|c_{\underline{K}}|^2 \left(1 - \frac{1}{(1+k^2)^2}\right)}{(E_1 - \frac{1}{4}k^2)^2} \right. \\
 &\quad + 16\pi \sum_{\underline{K}} \sum_{n=2}^5 \sum_{\text{odd } l} |c_{\underline{K}}|^2 (2l+1) (I_{n,1})^2 \left[ \frac{1}{(E_1 - E_n - \frac{1}{4}k^2)^2} - \frac{1}{(E_1 - \frac{1}{4}k^2)^2} \right] \Big\} \\
 &\quad + 16\pi \sum_{\underline{K}} \sum_{n=2}^5 \sum_{\text{odd } l} |c_{\underline{K}}|^2 (2l+1) (I_{n,1})^2 \frac{(E_n + \frac{1}{4}k^2)}{(E_1 - E_n - \frac{1}{4}k^2)^2} \\
 &\quad + \sum_{\underline{K}} \frac{\frac{1}{2}k^2 c_{\underline{K}}^2 \left(1 - \frac{1}{(1+k^2)^2}\right)}{(E_1 - \frac{1}{4}k^2)^2} - 16\pi \sum_{\underline{K}} \sum_{n=2}^5 \sum_{\text{odd } l} \frac{\frac{1}{4}k^2 |c_{\underline{K}}|^2 (2l+1) (I_{n,1})^2}{(E_1 - \frac{1}{4}k^2)^2}
 \end{aligned} \tag{3-8}$$

where  $I_{n,1} = \int_0^{\infty} R_{n1}(r) j_1\left(\frac{kr}{2}\right) \phi_{100}(r) r^2 dr$ ,  
 $R_{n1}(r)$  is the normalized radial part of  $\phi_{nlm}(r)$  and  
 $j_1\left(\frac{kr}{2}\right)$  is a spherical Bessel function.

### Results

Expressions (3-7) and (3-8) were evaluated on the I.B.M. 1620 computer. The result obtained for  $\mathcal{E} = \frac{(\psi|H|\psi)}{(\psi|\psi)}$  was -17.54 e.v..

## CHAPTER FOUR

### THE FIRST ELECTRON ENERGY GAP IN THE CRYSTAL

This chapter deals with the evaluation of the electronic energies at the top of the valence band and at the bottom of the conduction band in the crystal of lithium fluoride. The difference of these energies gives the energy gap at the boundary of the first Brillouin zone, which will be needed in the energetic considerations for positronium to form and persist in the crystal.

#### The Crystal Symmetry Group

Let us first examine the symmetries of the crystal. Since the crystal structure is face-centred<sup>-cubic,</sup> the crystal is invariant with respect to permutations and, or separate inversions of coordinate axes in the Cartesian system. Thus the symmetry of the crystal is determined by the assembly of all such combinations called symmetry transformations, the set of which altogether is called the symmetry group of the crystal. This group is of order 48. Let the generators of the group be denoted by

$E$  = identity element

$P_{xy}$  = element for interchange of X, Y axes

$P_{yz}$  = element for interchange of Y, Z axes

$P_{zx}$  = element for interchange of Z, X axes

$I_x$  = element for inversion of X-axis

$I_y$  = element for inversion of Y-axis

$I_z$  = element for inversion of Z-axis

We shall use the following related notations for the group elements:

$E \sim (X, Y, Z)$

$P_{xy} \sim (Y, X, Z)$

$P_{yz} \sim (X, Z, Y)$

$P_{zx} \sim (Z, Y, X)$

$I_x \sim (-X, Y, Z)$

$I_y \sim (X, -Y, Z)$

$I_z \sim (X, Y, -Z)$

In this notation, the 48 group elements are

(X, Y, Z) (X, Z, Y) (Z, Y, X) (Y, X, Z) (Z, X, Y) (Y, Z, X)  
(-X,-Y,-Z) (-X,-Z,-Y) (-Z,-Y,-X) (-Y,-X,-Z) (-Z,-X,-Y) (-Y,-Z,-X)  
(-X, Y,Z) (-X,Z, Y) (-Z,Y, X) (-Y,X, Z) (-Z,X, Y) (-Y,Z, X)  
(X,-Y, Z) (X,-Z, Y) (Z,-Y, X) (Y,-X, Z) (Z,-X, Y) (Y,-Z, X)  
(X, Y,-Z) (X, Z,-Y) (Z, Y,-X) (Y, X,-Z) (Z, X,-Y) (Y, Z,-X)  
(-X,-Y,Z) (-X,-Z,Y) (-Z,-Y,X) (-Y,-X,Z) (-Z,-X,Y) (-Y,-Z,X)  
(X,-Y,-Z) (X,-Z,-Y) (Z,-Y,-X) (Y,-X,-Z) (Z,-X,-Y) (Y,-Z,-X)  
(-X,Y,-Z) (-X,Z,-Y) (-Z,Y,-X) (-Y,X,-Z) (-Z,X,-Y) (-Y,Z,-X) (4-1)

In group theory, two elements  $g_1$  and  $g_2$  are said to be conjugate to each other if there exists an element  $g$  in the group such that

$$g_1 = g g_2 g^{-1}$$

All elements conjugate to each other form a set called a conjugate class with the following properties:

- (i) Each class is completely determined by any one element of it.
- (ii) We can divide the whole group into classes; each element of the group can appear in only one class.
- (iii) All elements of a given class are of the same order.

However, the converse may not be true.

- (iv) The simultaneous eigenfunctions of all the elements of the same conjugate class in a one-dimensional representation of the group have the same eigenvalues.

There are of course many other properties of a group and of conjugate classes, but only what is relevant to our present work is of interest. So only the proof of (iv) will be given, which is in fact rather trivial.

$$\begin{aligned} \text{Let } g_1 \psi &= g'_1 \psi \\ g_2 \psi &= g'_2 \psi \\ g \psi &= g' \psi \end{aligned}$$

such that  $g_1 = gg_2g^{-1}$

We have denoted the eigenvalues by prime.

$$g_1\psi = gg_2g^{-1}\psi = g'g'^{-1}g_2\psi = g_2'\psi$$

Since the representation is one-dimensional,  $\psi$  is non-degenerate.

$$\therefore g_1' = g_2'$$

q. e. d.

### The Choice of Trial Wavefunctions

Now consider the symmetry group in the crystal. The identity element E necessarily forms a conjugate class by itself.

$P_{xy}, P_{yz}, P_{zx}$  belong to the same conjugate class, for  $P_{zx}P_{xy}P_{zx}^{-1} = P_{zx}P_{xy}P_{zx} = P_{yz}$  etc..

Also,  $I_x, I_y, I_z$  belong to the same conjugate class, for  $P_{zx}I_xP_{zx}^{-1} = I_z$  etc..

However,  $I_x$ , etc. and  $P_{xy}$ , etc. do not belong to the same conjugate class, for if  $g$  is any element of the group, then consider  $gI_xg^{-1}$ . This is of odd inversion, while  $P_{xy}$  etc. are not.

Again, letting prime denote eigenvalues, since



$P_{xy}^2 = I_x^2 = E$ , the identity element, which is also true of the other generators of the group, we have

$$P'_{xy} = \pm 1 \text{ etc.}$$

$$I'_x = \pm 1 \text{ etc.}$$

Thus for one-dimensional representation, we have, by

(iv), only the following possibilities:

$$(1) \quad P'_{xy} = P'_{yz} = P'_{zx} = 1$$

$$I'_x = I'_y = I'_z = 1$$

$$(2) \quad P'_{xy} = P'_{yz} = P'_{zx} = -1$$

$$I'_x = I'_y = I'_z = 1$$

$$(3) \quad P'_{xy} = P'_{yz} = P'_{zx} = 1$$

$$I'_x = I'_y = I'_z = -1$$

$$(4) \quad P'_{xy} = P'_{yz} = P'_{zx} = -1$$

$$I'_x = I'_y = I'_z = -1$$

(4-2)

Now since a simultaneous eigenfunction of the generators of the group is automatically an eigenfunction of any element of the group, the eigenvalue of any element, then, is given by (4-2) together with the multiplication table.

We now come back to the physical problem. The wavefunction of an electron in the crystal can be written as a linear combination of wavefunctions of the Bloch type:

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} \varphi(\mathbf{r})$$

where  $\varphi(\underline{r})$  is periodic in the lattice. For our present interest,  $\underline{k}$  would be a vector ending on the boundary of the first Brillouin zone, i.e. it ends on the smallest envelope obtained by drawing planes perpendicular to and bisecting the reciprocal lattice vectors.

Let  $H$  be the Hamiltonian of the system (that is, the system of an electron moving in the crystal potential  $V(\underline{r})$ ).

$$H = -\frac{1}{2}\nabla^2 - V \quad (4-3)$$

Note that we have used atomic units (see Introduction).

Since  $\nabla^2$  and  $V$  are invariant under permutations and, or separate inversions of the  $X, Y, Z$  axes in the Cartesian system,  $H$  then commutes with the symmetry group, and we can seek a simultaneous eigenfunction of them. According to (4-2), there are four such possibilities. We shall denote each of the possibilities by the subscript or superscript  $i$  ( $i = 1, 2, 3, 4$ ) in accordance with the order given in (4-2), and when talking about anyone of them in general, no subscript or superscript will be used.

Let  $\Psi$  denote the trial electronic wavefunction. It is to be an eigenfunction of any element  $g$  of the crystal symmetry group. Denote the eigenvalue by  $\epsilon_g$ .

$$\therefore g\Psi = \epsilon_g \Psi \quad (4-4)$$

Also,  $\Psi$  has to be a linear combination of

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} \varphi(\mathbf{r}) \quad (4-5)$$

where  $\mathbf{k}$  ends on the first Brillouin zone boundary and  $\varphi(\mathbf{r})$  is periodic in the lattice. We assert that

$$\Psi = \sum_{\mathbf{g}} \epsilon_{\mathbf{g}} \mathbf{g} \psi \quad (4-6)$$

is a suitable trial wavefunction. To show this, we first prove the following:

(a) For one-dimensional representation of the group,

$$\epsilon_{g_1 g_2 g_3 \dots} = \epsilon_{g_1} \epsilon_{g_2} \epsilon_{g_3} \dots$$

Proof:

$$\begin{aligned} \epsilon_{g_1 g_2 g_3 \dots} \Psi &= (g_1 g_2 g_3 \dots) \Psi \\ &= g_1 g_2 g_3 \dots \Psi \\ &= \epsilon_{g_1} \epsilon_{g_2} \epsilon_{g_3} \dots \Psi \end{aligned}$$

q. e. d.

(b) If  $\psi$  as given in (4-5) is a Bloch-type wavefunction, then  $\mathbf{g}\psi$  is also a Bloch-type wavefunction with possibly a different  $\mathbf{k}$ , denoted by  $\mathbf{k}'$ , such that  $\mathbf{k}' = \mathbf{g}\mathbf{k}$ ,  $|\mathbf{k}'| = |\mathbf{k}|$ , and  $\mathbf{k}'$  also ends on the boundary of the first Brillouin zone as does  $\mathbf{k}$  in  $\psi$ .

Proof:

Let  $\underline{k} = \pi( m_1 \underline{b}_1 + m_2 \underline{b}_2 + m_3 \underline{b}_3 )$ , where  $\underline{b}_1, \underline{b}_2, \underline{b}_3$  are the three basic vectors of the reciprocal lattice, and  $m_1, m_2, m_3$  are some integers such that  $\underline{k}$  is the smallest vector in that direction. Then  $\underline{k}$  ends on the boundary of the first Brillouin zone.

Since  $\varphi(\underline{r})$  is periodic in the lattice, it can be Fourier analyzed as

$$\varphi(\underline{r}) = \sum_{\underline{K}} A_{\underline{K}} e^{2\pi i \underline{K} \cdot \underline{r}} \quad (4-7)$$

where  $\underline{K} = n_1 \underline{b}_1 + n_2 \underline{b}_2 + n_3 \underline{b}_3$  is a vector of the reciprocal lattice;  $n_1, n_2, n_3$  being integers.

Referring to fig. 2, we choose the three basic Bravais lattice vectors  $\underline{a}_1, \underline{a}_2, \underline{a}_3$  as the oblique coordinate axes whose unit vectors are represented by  $\underline{i}, \underline{j}$ , and  $\underline{k}$  respectively.

$$\therefore \psi = \sum_{n_1 n_2 n_3} \left[ A_{n_1 n_2 n_3} e^{\pi i (m_1 \underline{b}_1 + m_2 \underline{b}_2 + m_3 \underline{b}_3) \cdot (x \underline{i} + y \underline{j} + z \underline{k})} \times e^{2\pi i (n_1 \underline{b}_1 + n_2 \underline{b}_2 + n_3 \underline{b}_3) \cdot (x \underline{i} + y \underline{j} + z \underline{k})} \right] \quad (4-8)$$

Since  $\underline{i} = \frac{\underline{a}_1}{|\underline{a}_1|} = \frac{\underline{a}_1}{\sqrt{2L}}$  etc., where  $L$  is the distance

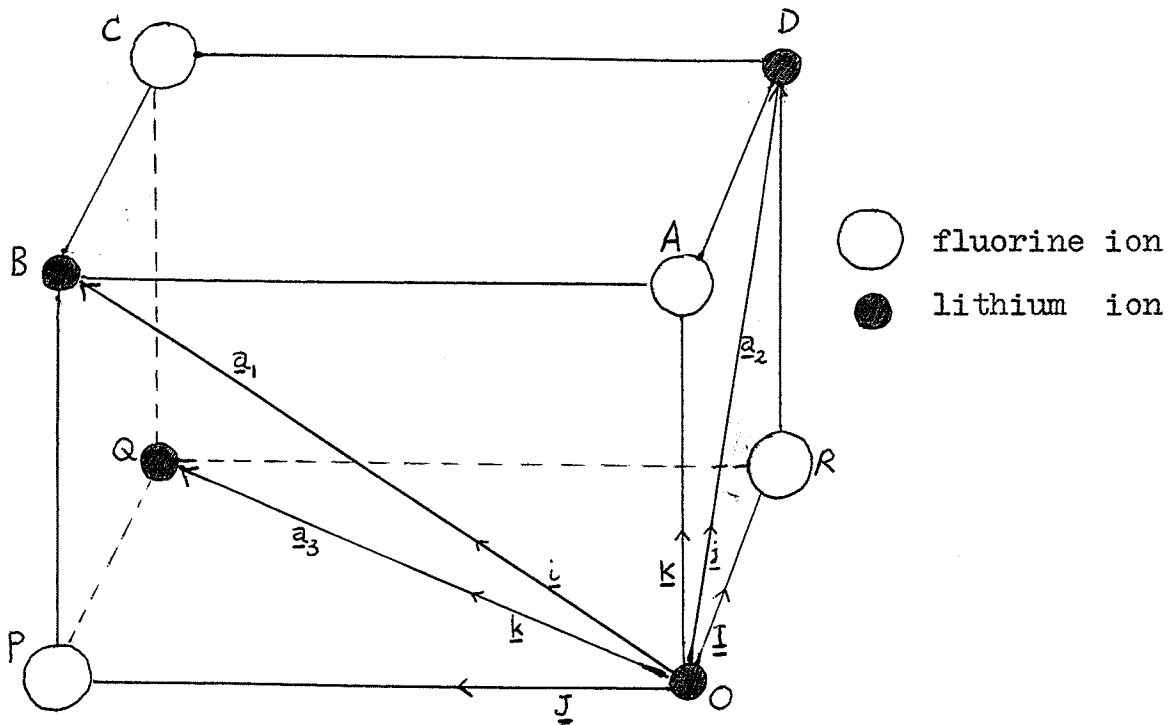


fig. 2

The lithium fluoride crystal

between a positive ion and its nearest negative ion, and since  $\underline{a}_\lambda \cdot \underline{b}_\mu = \delta_{\lambda\mu}$ , we have

$$\psi = \sum_{n_1 n_2 n_3} A_{n_1 n_2 n_3} e^{\frac{\pi i}{\sqrt{2}L}(m_1 x + m_2 y + m_3 z)} e^{\frac{2\pi i}{\sqrt{2}L}(n_1 x + n_2 y + n_3 z)} \quad (4-9)$$

We have used small letters to represent oblique coordinate system. We now let capital letters represent

Cartesian system ( see fig 2 )

$$\begin{aligned} \therefore \underline{r} &= X\underline{I} + Y\underline{J} + Z\underline{K} \\ &= x\underline{i} + y\underline{j} + z\underline{k} \end{aligned}$$

$$\begin{aligned} \text{But } \underline{i} &= (\underline{J} + \underline{K})/\sqrt{2} \\ \underline{j} &= (\underline{K} + \underline{I})/\sqrt{2} \\ \underline{k} &= (\underline{I} + \underline{J})/\sqrt{2} \end{aligned}$$

$$\begin{aligned} \therefore x &= \frac{1}{2}(Y + Z - X) \\ y &= \frac{1}{2}(Z + X - Y) \\ z &= \frac{1}{2}(X + Y - Z) \end{aligned}$$

$$\therefore \psi = \sum_{N_1 N_2 N_3} A_{N_1 N_2 N_3} e^{\frac{\pi i}{L} [(N_1 + M_1)X + (N_2 + M_2)Y + (N_3 + M_3)Z]} \quad (4-10)$$

$$\text{where } N_1 = n_2 + n_3 - n_1$$

$$N_2 = n_3 + n_1 - n_2$$

$$N_3 = n_1 + n_2 - n_3$$

$$M_1 = \frac{1}{2}(m_2 + m_3 - m_1)$$

$$M_2 = \frac{1}{2}(m_3 + m_1 - m_2)$$

$$M_3 = \frac{1}{2}(m_1 + m_2 - m_3) \quad (4-11)$$

Consider  $g$  operating on  $\psi$  .

$$g\psi = g \left[ e^{i\mathbf{k} \cdot \underline{r}} \varphi(\underline{r}) \right]$$

$$\begin{aligned}
&= \left[ g e^{i \underline{k} \cdot \underline{r}} \right] \left[ g \varphi(\underline{r}) \right] \\
&= e^{i g \underline{k} \cdot \underline{r}} g \varphi(\underline{r}) \\
&= e^{i \underline{k}' \cdot \underline{r}} \varphi'(\underline{r})
\end{aligned} \tag{4-12}$$

where  $\underline{k}' = g \underline{k}$ ,  $\varphi'(\underline{r}) = g \varphi(\underline{r})$

Since  $g$  is unitary,  $|\underline{k}'| = |\underline{k}|$ .

For  $g = P_{xy}$ ,

$$\begin{aligned}
P_{xy} \underline{k} &= P_{xy} \left[ \frac{\pi}{L} (M_1 \underline{I} + M_2 \underline{J} + M_3 \underline{K}) \right] \\
&= \frac{\pi}{L} (M_2 \underline{I} + M_1 \underline{J} + M_3 \underline{K}) \\
&= \underline{k}'
\end{aligned} \tag{4-13}$$

By (4-11), (4-13) can be written as

$$\underline{k}' = \pi (m_2 \underline{b}_1 + m_1 \underline{b}_2 + m_3 \underline{b}_3) \tag{4-14}$$

$$\begin{aligned}
P_{xy} \varphi(\underline{r}) &= P_{xy} \sum_{N_1 N_2 N_3} A_{N_1 N_2 N_3} e^{\frac{\pi i}{L} (N_1 X + N_2 Y + N_3 Z)} \\
&= \sum_{N_1 N_2 N_3} A_{N_1 N_2 N_3} e^{\frac{\pi i}{L} (N_2 X + N_1 Y + N_3 Z)} \\
&= \sum_{N_1 N_2 N_3} A_{\dot{N}_1 N_2 N_3} e^{\frac{\pi i}{L} (N_1 X + N_2 Y + N_3 Z)} \\
&= \varphi'(\underline{r}),
\end{aligned} \tag{4-15}$$

where  $A_{\dot{N}_1 N_2 N_3}$  is equal to some  $A_{\underline{K}}$  with possibly a different ordered set of  $N_1 N_2 N_3$ .

$\therefore P_{xy} \psi = e^{i \underline{k}' \cdot \underline{r}} \varphi'(\underline{r})$ , where  $\varphi'(\underline{r})$  is periodic in

the lattice, hence is the periodic part of a Bloch function.

Similar arguments hold for  $P_{yz}$  and  $P_{zx}$ .

Consider now the inversion  $I_x$ .

$$\begin{aligned} I_x \underline{k} &= \frac{\pi}{L} (-M_1 \underline{I} + M_2 \underline{J} + M_3 \underline{K}) \\ &= \underline{k}' \end{aligned} \quad (4-16)$$

By (4-11), (4-16) can be written as

$$\underline{k}' = \pi \left[ m_1 \underline{b}_1 + (m_1 - m_3) \underline{b}_2 + (m_1 - m_2) \underline{b}_3 \right] \quad (4-17)$$

$$\begin{aligned} I_x \psi(\underline{r}) &= \sum_{N_1 N_2 N_3} A_{N_1 N_2 N_3} e^{\frac{\pi i}{L} (-N_1 X + N_2 Y + N_3 Z)} \\ &= \sum_{N_1 N_2 N_3} A_{N_1 N_2 N_3} e^{\frac{\pi i}{L} (N_1 X + N_2 Y + N_3 Z)} \\ &= \psi'(\underline{r}), \end{aligned} \quad (4-18)$$

where again  $A_{N_1 N_2 N_3}$  is in general not equal to  $A_{N_1 N_2 N_3}$ , but is equal to some  $A_{\underline{K}}$  with possibly a different ordered set for  $\underline{K}$ . Hence  $I_x \psi$  is also a Bloch wavefunction.

Similar arguments hold for  $I_y$  and  $I_z$ .

It remains now to show that  $\underline{k}'$  in (4-14) or in (4-17) ends on the boundary of the first Brillouin zone.

As given by the form in (4-14) or (4-17),  $\underline{k}'$  is



either a vector of the reciprocal lattice or half integral multiple of one. Thus it either ends on the first Brillouin zone boundary or passes through it. Let us assume the latter case. Then there exists an integer  $c > 1$  such that for (4-14),

$$\underline{k}'/c = \pi(\underline{b}_1 m_2/c + \underline{b}_2 m_1/c + \underline{b}_3 m_3/c)$$

will end on the first Brillouin zone boundary, hence, is half a reciprocal lattice vector.

$\therefore m_2/c, m_1/c, m_3/c$  are integers.

Then  $\underline{k}/c = \pi(\underline{b}_1 m_1/c + \underline{b}_2 m_2/c + \underline{b}_3 m_3/c)$  is also half a reciprocal lattice vector. But it is smaller than  $\underline{k}$ , and yet they are in the same direction, hence a contradiction.

Similarly, assume there exists an integer  $d > 1$  such that for (4-17),

$$\underline{k}'/d = \pi \left[ \underline{b}_1 m_1/d + \underline{b}_2 (m_1 - m_3)/d + \underline{b}_3 (m_1 - m_2)/d \right]$$

is half a reciprocal lattice vector ending on the first Brillouin zone boundary.

$\therefore m_1/d, (m_1 - m_3)/d, (m_1 - m_2)/d$  are integers.

Or,  $m_1/d, m_2/d, m_3/d$  are integers, which again lead to contradiction. Hence we conclude that  $\underline{k}'$  in (4-14) or (4-17) must end on the first Brillouin zone boundary.

Since  $I_x$ ,  $P_{xy}$  etc. generate the whole symmetry group, (b) is then proved.

q. e. d.

We now proceed to show that (4-6) is a suitable trial wavefunction.

Since for each  $g$  of the crystal symmetry group,  $g\psi$  has been shown to be a Bloch function at the boundary of the first Brillouin zone, (4-6) is a linear combination of such functions. We are here interested in obtaining a trial wavefunction of an electron at such a boundary, hence such a linear combination is a very suitable one for our purpose. Also, since the Hamiltonian of the electron in the crystal commutes with all the elements of the symmetry group, we can seek a simultaneous eigenfunction of the Hamiltonian and the group elements. The most suitable choice of trial wavefunction, therefore, would be one which is a simultaneous eigenfunction of the group elements. This is true of (4-6), for, if  $g_1$  is any element of the group, we can show that  $g_1\Psi = \epsilon_{g_1}\Psi$ .

Proof:

$$\begin{aligned} g_1\Psi &= g_1 \sum_g \epsilon_g g\psi \\ &= \sum_g \epsilon_g g_1 g\psi \\ &= \sum_g (\epsilon_{g_1 g} / \epsilon_{g_1}) g_1 g\psi \end{aligned}$$

$$\begin{aligned}
&= \epsilon_{g_1} \sum_g \epsilon_g g \psi \\
&= \epsilon_{g_1} \Psi
\end{aligned}$$

In the above proof, use has been made of (a), p. 24, and the facts that  $\epsilon_g = +1$  or  $-1$  so that  $\epsilon_g = 1/\epsilon_g$ , and that  $\sum_g f(g_1 g) = \sum_g f(g)$ .

q. e. d.

Thus we have now obtained our electronic trial wavefunction

$$\Psi = \sum_g \epsilon_g g \psi$$

where  $\psi = e^{i\mathbf{k} \cdot \mathbf{r}} \varphi(\mathbf{r})$

and  $\epsilon_g = +1$  or  $-1$ .

} (4-19)

The question now arises as to which value of  $\mathbf{k}$  should be chosen.

Since  $\mathbf{k} = \pi(m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3)$  ends on the first Brillouin zone boundary, and since  $e^{2\pi i \mathbf{b}_\mu \cdot \mathbf{r}}$ , where  $\mu = 1, 2$  or  $3$ , is periodic in the lattice, hence can be transferred to the periodic part of the Bloch function, the possible values that  $m_\mu$  can take are 0 or 1, which is exhaustive. Thus we have the following possibilities:

$$\underline{k} = \pi \underline{b}_\mu, \quad \mu = 1, 2 \text{ or } 3 \quad (4-20)$$

$$\underline{k} = \pi(\underline{b}_\mu + \underline{b}_\nu), \quad \mu, \nu = 1, 2 \text{ or } 3, \mu \neq \nu \quad (4-21)$$

$$\underline{k} = \pi(\underline{b}_1 + \underline{b}_2 + \underline{b}_3) \quad (4-22)$$

For  $\mu = 1$ , (4-20) becomes

$$\underline{k} = \frac{\pi}{2L}(\underline{J} + \underline{K} - \underline{I}) \quad (4-23)$$

and (4-22) can be re-written as

$$\underline{k} = \frac{\pi}{2L}(\underline{I} + \underline{J} + \underline{K}) \quad (4-24)$$

(4-23) and (4-24) are in fact equivalent up to a transformation by some group element, hence are also (4-20) and (4-22) in general.

For  $\mu = 1, \nu = 2$ , (4-21) becomes

$$\underline{k} = \frac{\pi}{L}\underline{K} \quad (4-25)$$

Thus, (4-21) corresponds to directions along the three coordinate axes.

In fig. 3, the Cartesian axes  $\underline{I}$ ,  $\underline{J}$  and  $\underline{K}$  pass through the centres of the squares. A choice of  $\underline{k}$  as given in (4-20) or (4-22) is a vector ending on the centre of one of the 8 hexagons, while that given by (4-21) ends on the centre of one of the 6 squares. We will argue qualitatively as to which  $\underline{k}$  to choose. The expression (4-20) corresponds to a  $\underline{k}$  in the direction of a diagonal OC in fig. 2 while the expression (4-21)

corresponds to a direction in which positive and negative ions are closest together. Hence an electron moving in the former direction has on the average lower energy than that moving in the other directions. Also, it needs less energy to excite an electron in the former direction where the electrostatic force on the average is smaller. Hence the band structure is <sup>qualitatively</sup> ~~roughly~~ like that shown in fig. 4.

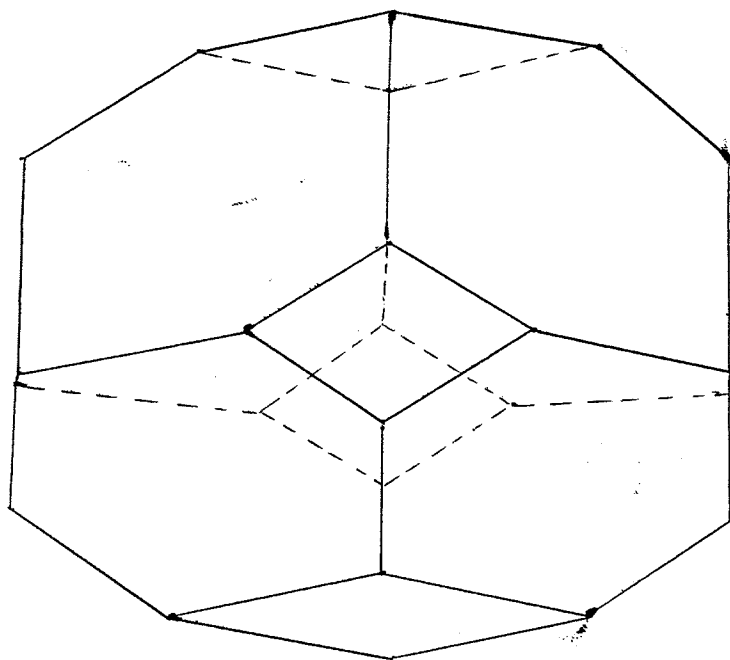


fig. 3

The first Brillouin Zone of lithium fluoride

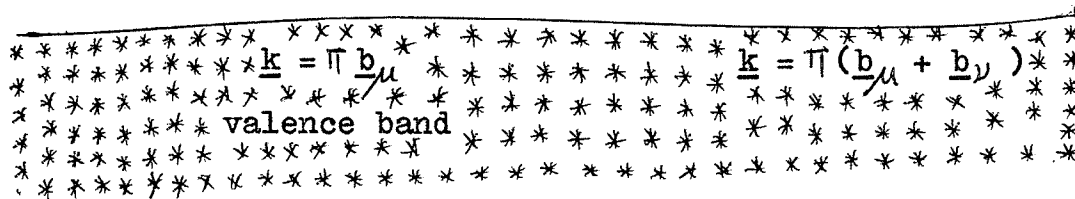
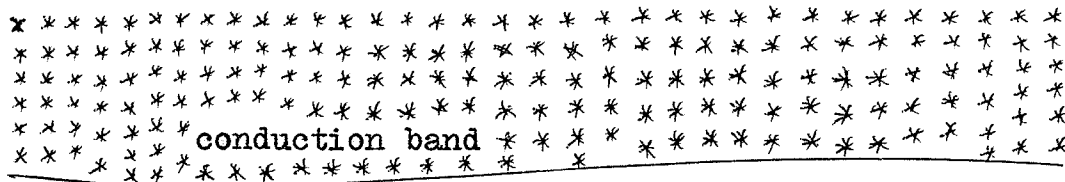


fig. 4

A rough diagram showing electronic band structure in LiF

We would like to get the smallest gap. Although we are inclined to believe that the gap varies little with directions of  $\underline{k}$ , we will, however, choose

$$\underline{k} = \pi \underline{b}_1 \tag{4-26}$$

Therefore, the trial electronic wavefunction is given by

$$\Psi = \sum_{\mathbf{g}} \epsilon_{\mathbf{g}} g \psi$$

$$\psi = \sum_{N_1 N_2 N_3} A_{N_1 N_2 N_3} e^{\frac{\pi i}{L} [(N_1 - \frac{1}{2})X + (N_2 + \frac{1}{2})Y + (N_3 + \frac{1}{2})Z]}$$

$\left. \vphantom{\sum_{N_1 N_2 N_3}} \right\} (4-27)$

with  $N_1 = n_2 + n_3 - n_1$   
 $N_2 = n_3 + n_1 - n_2$

$$N_3 = n_1 + n_2 - n_3, \quad ]$$

where (4-10), (4-11) and (4-23) have been used. In the above,  $n_1, n_2, n_3$  are integers, hence are also  $N_1, N_2, N_3$ . Moreover,  $N_1+N_2, N_2+N_3, N_3+N_1$  must all be even, or  $N_1, N_2$  and  $N_3$  must have the same parity.

$$\text{Write } \mathcal{N}_1 = N_1 - \frac{1}{2}$$

$$\mathcal{N}_2 = N_2 + \frac{1}{2}$$

$$\mathcal{N}_3 = N_3 + \frac{1}{2}$$

$\therefore$  (4-27) becomes

$$\Psi = \sum_{\mathcal{N}_1 \mathcal{N}_2 \mathcal{N}_3} A_{\mathcal{N}_1 \mathcal{N}_2 \mathcal{N}_3} e^{\frac{\pi i}{L}(\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)} \quad (4-28)$$

where  $\mathcal{N}_1, \mathcal{N}_2, \mathcal{N}_3$  ( afterwards referred to either individually or as a set as  $\mathcal{N}$  ) run through half-integers.

$$\therefore \Psi = \sum_{\mathcal{N}} A_{\mathcal{N}} \sum_{\mathbf{g}} \epsilon_{\mathbf{g}} e^{i \frac{\pi}{L}(\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)} \quad (4-29)$$

Before going on further, it is interesting to note that with the origin chosen at a positive ion site, which has been the case all along,  $\Psi_1, \Psi_2, \Psi_3$  and  $\Psi_4$  all vanish at the point  $(L, 0, 0)$ , which is a negative ion site. This tells further that our trial wavefunctions are suitable ones. For, an electron must be least likely to be found at the negative ion sites, because of the strong Coulomb repulsion there.

Now we introduce the notation that  $g$  written in front of a bracket means that it permutes, and, or inverts, depending on what the element  $g$  is, the  $X$ ,  $Y$ ,  $Z$  inside the bracket, or their coefficients, whichever way we like. Also a permutation or inversion of the ordered set  $\mathcal{N}$  by  $g$  will be represented by  $g(\mathcal{N})$ .

Consider our final form of the electronic trial wavefunction given by (4-29). For any term due to the ordered set  $\mathcal{N}$ , we also have a term due to  $g'(\mathcal{N})$  where  $g'$  is any group element. This latter term is equal to

$$\begin{aligned}
 & A_{g'(\mathcal{N})} \sum_g \epsilon_g g e^{\frac{\pi i}{L} g(\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)} \\
 &= A_{g'(\mathcal{N})} \sum_g \epsilon_g g g' e^{\frac{\pi i}{L} (\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)} \\
 &= A_{g'(\mathcal{N})} \sum_g (\epsilon_{g g'} / \epsilon_{g'}) g g' e^{\frac{i}{L} (\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)} \\
 &= \epsilon_{g'} A_{g'(\mathcal{N})} \sum_g \epsilon_g g e^{\frac{\pi i}{L} (\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)} \\
 &= \text{a constant times } A_{\mathcal{N}} \sum_g \epsilon_g g e^{\frac{\pi i}{L} (\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)}
 \end{aligned}$$

Hence we can suppress this constant, and in (4-29), the



summation over  $\mathcal{N}$  will be carried out only once for any set  $\{g(\mathcal{N})\}$ . We make the rule that we shall sum for  $\mathcal{N}_1 \geq \mathcal{N}_2 \geq \mathcal{N}_3 \geq 0$  only. We recall that  $\mathcal{N}_1, \mathcal{N}_2, \mathcal{N}_3$  must all be half integers. There is otherwise no restriction for them. Now define

$$\phi_{\mathcal{N}} = e^{\frac{\pi i}{L}(\mathcal{N}_1 X + \mathcal{N}_2 Y + \mathcal{N}_3 Z)} \quad (4-30)$$

$$\chi_{\mathcal{N}} = \sum_{\mathbf{g}} \epsilon_{\mathbf{g}} g \phi_{\mathcal{N}} \quad (4-31)$$

$$\therefore \Psi = \sum_{\mathcal{N}} A_{\mathcal{N}} \chi_{\mathcal{N}} \quad (4-32)$$

Evaluation of electron energies at the first Brillouin zone boundary.

The energy of an electron at the first Brillouin zone boundary in the crystal can be approximated by an upper bound, which is the minimum value of

$$\mathcal{E} = \frac{(\Psi | H | \Psi)}{(\Psi | \Psi)} \quad (4-33)$$

There are according to (4-2) four trial wavefunctions. Minimizing (4-33) for each, we expect to get two different minimum values for  $\mathcal{E}$ , one corresponds to an upper bound to the top of the valence band, the other to the bottom of the

conduction band.

$\Psi$  as given by (4-32) can be thought of as a linear combination of  $\chi_{\mathcal{N}}$ , or even, of  $\phi_{\mathcal{N}}$ . Now the Hamiltonian  $H$  (see (4-3)) is hermitian. Hence the matrix (or rather, the submatrix, since in the evaluation, only a finite number of  $\chi_{\mathcal{N}}$  is taken) for  $H$ , which is real as will be shown below, is symmetric.

So far we have not used a normalized basis. We will now normalize  $\chi_{\mathcal{N}}$ .

$$\begin{aligned}
 (\chi_{\mathcal{N}} | \chi_{\mathcal{N}'}) &= \sum_{\mathcal{g}} \sum_{\mathcal{g}'} \epsilon_{\mathcal{g}} \epsilon_{\mathcal{g}'} (\mathcal{g} \phi_{\mathcal{N}} | \mathcal{g}' \phi_{\mathcal{N}'}) \\
 &= \sum_{\mathcal{g}} \sum_{\mathcal{g}'} \epsilon_{\mathcal{g}} \epsilon_{\mathcal{g}'} (\phi_{\mathcal{N}} | \mathcal{g}^{-1} \mathcal{g}' | \phi_{\mathcal{N}'}) \\
 &= \sum_{\mathcal{g}} \sum_{\mathcal{g}'} \epsilon_{\mathcal{g}}^{-1} \epsilon_{\mathcal{g}'} (\phi_{\mathcal{N}} | \mathcal{g}^{-1} \mathcal{g}' | \phi_{\mathcal{N}'}) \\
 &= 48 \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} (\phi_{\mathcal{N}} | \mathcal{g} | \phi_{\mathcal{N}'}) \\
 &= 48 \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \delta_{\mathcal{N}, \mathcal{g}(\mathcal{N}')} , \tag{4-34}
 \end{aligned}$$

where use has been made of the unitary property of the group elements, and the delta notation has the usual meaning. That is,

$$\delta_{i,j} = 0 \quad \text{if } i \neq j$$

$$\delta_{i,j} = 1 \quad \text{if } i = j$$

From now on, therefore, for normalization, we write

$$\chi_{\mathcal{N}} = \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \mathcal{g} \phi_{\mathcal{N}} / (48 \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \delta_{\mathcal{N},\mathcal{g}})^{\frac{1}{2}} \quad (4-35)$$

$$\therefore (\Psi | \Psi) = \sum_{\mathcal{N}} |A_{\mathcal{N}}|^2 \quad (4-36)$$

$$(\Psi | H | \Psi) = \sum_{\mathcal{N}} \sum_{\mathcal{N}'} A_{\mathcal{N}}^* A_{\mathcal{N}'} (\chi_{\mathcal{N}} | H | \chi_{\mathcal{N}'}) \quad (4-37)$$

$$(\chi_{\mathcal{N}} | H | \chi_{\mathcal{N}'}) = (\chi_{\mathcal{N}} | -\frac{1}{2}\nabla^2 | \chi_{\mathcal{N}'}) + (\chi_{\mathcal{N}} | -V | \chi_{\mathcal{N}'}) \quad (4-38)$$

$$\begin{aligned} (\chi_{\mathcal{N}} | -\frac{1}{2}\nabla^2 | \chi_{\mathcal{N}'}) &= (-\frac{1}{2}) \left( \frac{\pi i}{L} \right)^2 (\mathcal{N}'_1{}^2 + \mathcal{N}'_2{}^2 + \mathcal{N}'_3{}^2) (\chi_{\mathcal{N}} | \chi_{\mathcal{N}'}) \\ &= \frac{\pi^2}{2L^2} (\mathcal{N}'_1{}^2 + \mathcal{N}'_2{}^2 + \mathcal{N}'_3{}^2) \delta_{\mathcal{N},\mathcal{N}'} \end{aligned} \quad (4-39)$$

$$\begin{aligned} (\chi_{\mathcal{N}} | -V | \chi_{\mathcal{N}'}) &= -48 \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} (\phi_{\mathcal{N}} | V \mathcal{g} | \phi_{\mathcal{N}'}) / \left\{ \left[ 48 \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \delta_{\mathcal{N},\mathcal{g}}(\mathcal{N}) \right]^{\frac{1}{2}} \left[ 48 \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \delta_{\mathcal{N}',\mathcal{g}}(\mathcal{N}') \right]^{\frac{1}{2}} \right\} \\ &= - \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \mathcal{g} (\phi_{\mathcal{N}} | V | \phi_{\mathcal{N}'}) / \left\{ \left[ \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \delta_{\mathcal{N},\mathcal{g}}(\mathcal{N}) \right]^{\frac{1}{2}} \left[ \sum_{\mathcal{g}} \epsilon_{\mathcal{g}} \delta_{\mathcal{N}',\mathcal{g}}(\mathcal{N}') \right]^{\frac{1}{2}} \right\}, \end{aligned} \quad (4-40)$$

where  $\mathcal{g}$  in the numerator operates only on  $\mathcal{N}'$ .

$$(\phi_{\mathcal{N}} | V | \phi_{\mathcal{N}'}) = \text{Lim}_{S \rightarrow \infty} \frac{1}{S^3} \int_{\mathcal{V}} \text{ve}^{\frac{\pi i}{L} [(\mathcal{N}'_1 - \mathcal{N}_1)X + (\mathcal{N}'_2 - \mathcal{N}_2)Y + (\mathcal{N}'_3 - \mathcal{N}_3)Z]} d\tau \quad (4-41)$$

This is in fact the Fourier coefficient of  $V$ , except that unlike (2-14), it is now in units of  $e^2/a_0$  rather than  $e/a_0$ . (2-14) can be written as

$$C_{n_1 n_2 n_3} = C_{N_1 N_2 N_3} = \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\tau} V e^{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)} d\tau$$

$$= \frac{2\pi}{L^3} \left[ \frac{2}{k^2 + \alpha^2} + \frac{1}{k^2} + (-1)^{n_1 + n_2 + n_3} \left( \frac{4.7}{k^2 + \beta^2} - \frac{1}{k^2} \right) \right]. \quad (4-42)$$

where  $N_1 = n_2 + n_3 - n_1$

$$N_2 = n_3 + n_1 - n_2$$

$$N_3 = n_1 + n_2 - n_3$$

and

$$k^2 = \frac{\pi^2}{L^2} (N_1^2 + N_2^2 + N_3^2).$$

$\therefore C_{N_1 N_2 N_3}$  is invariant with respect to any transformation, belonging to the symmetry group, of the subscripts.

$$\therefore (\phi_{N'} | V | \phi_N) = C_{N'_1 - N_1, N'_2 - N_2, N'_3 - N_3}, \text{ which is abbreviated to } C_{N' - N}.$$

$$\therefore (\Psi | H | \Psi) = \sum_N \sum_{N'} A_N^* A_{N'} \alpha_{NN'}, \quad (4-43)$$

$$\text{where } \alpha_{NN'} = \frac{\pi^2}{2L^2} (N_1^2 + N_2^2 + N_3^2) \left\{ \frac{\sum_g \epsilon_g C_{N-g(N')}}{\left[ \sum_g \epsilon_g \delta_{N, g(N')} \right]^{\frac{1}{2}} \left[ \sum_g \epsilon_g \delta_{N', g(N')} \right]^{\frac{1}{2}}} \right\} \quad (4-44)$$



We now proceed to minimize  $\xi = \frac{(\Psi|H|\Psi)}{(\Psi|\Psi)}$  with respect to the parameters  $A_{\mathcal{N}}^*$ .

Our problem then is the same as finding the extremum of  $(\Psi|H|\Psi)$  subject to the condition that  $(\Psi|\Psi) = 1$ . Thus we set

$$\frac{\partial}{\partial A_{\mathcal{N}}^*} \left[ (\Psi|H|\Psi) - \lambda (\Psi|\Psi) \right] = 0 \quad \text{for each } \mathcal{N} \quad (4-45)$$

Then (4-36) and (4-43) give us

$$\sum_{\mathcal{N}'} \alpha_{\mathcal{N}\mathcal{N}'} A_{\mathcal{N}'} - \lambda A_{\mathcal{N}} = 0 \quad \text{for each } \mathcal{N} \quad (4-46)$$

We can make a convention to label  $A_{\mathcal{N}}$ , so that

(4-46) is equivalent to

$$\alpha \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \end{pmatrix} = \lambda \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \end{pmatrix} \quad (4-47)$$

where  $\alpha = (\alpha_{\mathcal{N}\mathcal{N}'})$  is in fact a matrix representation of the Hamiltonian  $H$  with respect to  $\mathcal{X}_{\mathcal{N}}$ , as is clear by comparing (4-43) and (4-37). Since  $\alpha$  is hermitian and real, it is symmetric. (4-47) then is equivalent to

$$H \Psi = \xi \Psi \quad (4-48)$$

Therefore the minimum value of  $\xi$  is the same as the smallest solution of  $\lambda$  in (4-47).

Correction due to shift of origin of the crystal potential.

Since a crystal on the whole is electrically neutral, the average value of the crystal potential over space should be zero. This is, however, not true of our representation by (2-11). The latter can be written as

$$V = V_0 + V_{\text{shift}} \quad (4-49)$$

where  $V_0$  is the potential with the right origin, so that its average over space vanishes, and  $V_{\text{shift}}$ , a constant, is the shift of the crystal potential. Integrating (4-49) over space, we have

$$\begin{aligned} V_{\text{shift}} &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\mathcal{V}_R} V \, d\mathcal{V}_R \\ &= C_{000} \\ &= \frac{2\pi}{L^3} \left[ \frac{2}{\alpha^2} + \frac{4.7}{\beta^2} \right] \\ &= 12.08 \text{ e.v.} \end{aligned}$$

Write the Hamiltonian as

$$H = H_0 + H_{\text{shift}} \quad (4-50)$$

where  $H_0$  is the Hamiltonian with the right origin. We have for the case of an electron,  $H_{\text{shift}} = -V_{\text{shift}} = -12.08 \text{ e.v.}$

and for the case of a positron,  $H_{\text{shift}} = + V_{\text{shift}} = 12.08 \text{ e.v.}$

$$\frac{(\Psi|H_0|\Psi)}{(\Psi|\Psi)} = \frac{(\Psi|H|\Psi)}{(\Psi|\Psi)} - H_{\text{shift}} \quad (4-51)$$

For the case of an electron, therefore,

$$\frac{(\Psi|H_0|\Psi)}{(\Psi|\Psi)} = \frac{(\Psi|H|\Psi)}{(\Psi|\Psi)} + 12.08 \text{ e.v.} \quad (4-52)$$

For the case of a positron,

$$\frac{(\Psi|H_0|\Psi)}{(\Psi|\Psi)} = \frac{(\Psi|H|\Psi)}{(\Psi|\Psi)} - 12.08 \text{ e.v.} \quad (4-53)$$

### Results

The eigenvalue problem in (4-47) can be solved by diagonalizing the symmetry matrix  $\alpha$ . The computation of the matrix elements and the diagonalization of the matrix were done on the I.B.M. 1620 computer for the trial wavefunctions  $\Psi_1$  and  $\Psi_3$ , the choice being a tentative one. The electron energies at the top of the valence band and at the bottom of the conduction band were obtained as  $-17.03 \text{ e.v.}$  and  $-8.14 \text{ e.v.}$  respectively, giving a gap of  $8.89 \text{ e.v.}$

CHAPTER FIVE

THE GROUND STATE ENERGY OF A POSITRON IN THE CRYSTAL

The wavefunction of a positron in the crystal, as for an electron, is a linear combination of Bloch wavefunctions of the form

$$\psi_{\underline{k}} = e^{i\underline{k} \cdot \underline{r}} \varphi(\underline{r}) \quad (5-1)$$

where  $\varphi(\underline{r})$  has the periodicity of the lattice.

(5-1) is an eigenfunction with eigenvalue  $E_{\underline{k}}$  satisfying

$$H \psi_{\underline{k}} = E_{\underline{k}} \psi_{\underline{k}} \quad (5-2)$$

where  $H$  is the Hamiltonian of the system of a positron moving in the crystal. For the ground state,  $\underline{k} = 0$ , so that we have

$$H \psi_{\underline{0}} = E_{\underline{0}} \psi_{\underline{0}} \quad (5-3)$$

$\psi_{\underline{0}}$  then has the periodicity of the lattice. We will now seek our trial wavefunction. Since the ground state should have maximum symmetry, a suitable trial wavefunction  $\Psi_0$  would be one which in the first place is periodic in the lattice, and secondly, we must require  $g\Psi_0 = \Psi_0$  for all  $g$  belonging to the symmetry group.

Since any periodic function can be Fourier analyzed, we can take  $\Psi_0$  to be of the form (4-7), <sup>which</sup> ~~hence~~ can be written as

$$\Psi_0 = \sum_{N_1 N_2 N_3} A_{N_1 N_2 N_3} e^{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)} \quad (5-4)$$



where  $N_1, N_2, N_3$  each runs through all integers, but they must have the same parity. (5-4) can also be written as

$$\Psi_0 = \sum_N \sum_g A_{g(N)} g e^{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)} \quad (5-5)$$

where the summation over  $N$  will be carried out only once for any set  $\{g(N)\}$ , the convention being  $N_1 \geq N_2 \geq N_3 \geq 0$ .

Now impose the condition that for any group element  $g_1$ ,  $g_1 \Psi_0 = \Psi_0$ .

$$\begin{aligned} \therefore g_1 \Psi_0 &= \sum_N \sum_g A_{g(N)} g_1 g e^{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)} \\ &= \sum_N \sum_g A_{g_1^{-1}g(N)} g e^{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)} \end{aligned} \quad (5-6)$$

Subtracting (5-6) from (5-5) and then ~~multiplied~~ <sup>multiplying</sup> by  $\left[ g_1 \exp\left\{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)\right\} \right]^+$ , and integrating, we have

$$A_{g_1(N)} = A_N \quad (5-7)$$

Since  $g_1$  is arbitrary, we have in general,

$$A_{g(N)} = A_N \quad (5-8)$$

where  $g$  is any element belonging to the symmetry group.

$$\therefore \Psi_0 = \sum_N A_N \sum_g g e^{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)} \quad (5-9)$$

Proceeding as in chapter 4, we write

$$\Psi_0 = \sum_N A_N \chi_N \quad (5-10)$$

where  $\chi_N = \sum_g g \phi_N$  (5-11)

$$\phi_N = e^{\frac{\pi i}{L}(N_1 X + N_2 Y + N_3 Z)} \quad (5-12)$$

$$\therefore (\Psi_0 | \Psi_0) = \sum_N |A_N|^2 \quad (5-13)$$

$$(\Psi_0 | H | \Psi_0) = \sum_N \sum_{N'} A_N A_{N'} \alpha_{NN'} \quad (5-14)$$

where  $\alpha_{NN'} = \frac{\pi^2}{2L^2} (N_1^2 + N_2^2 + N_3^2) \delta_{N,N'}$

$$+ \frac{\sum_g C_{N-g(N')}}{\left[ \sum_g \delta_{N,g(N)} \right]^{\frac{1}{2}} \left[ \sum_g \delta_{N';g(N')} \right]^{\frac{1}{2}}} \quad (5-15)$$

Notice that unlike the case of the electron, there is a sign change in (5-15). Also, N here is a set of integers of the same parity while the  $\mathcal{N}$  in (4-44) are half integers.

Now our trial wavefunction  $\Psi_0$  as given by (5-9) is not vanishingly small at the origin, which, therefore, cannot be a positive ion site. For the origin to be at a negative ion

site, the Fourier coefficients of the crystal potential will be given by

$$C_{\underline{K}} = \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\tau_R} e^{-2\pi i \underline{K} \cdot \underline{R}} \sum_j \left[ v_1(\underline{R} - \underline{R}_j - \underline{a}) + v_2(\underline{R} - \underline{R}_j) \right] d\tau_R \quad (5-16)$$

where now  $\underline{R}_j$  is the position vector of the  $j$ th negative ion and  $\underline{a}$  is the position vector of a positive ion with respect to the origin. (compare (5-16) with (2-11))

Following the same way of evaluation as before, (5-16) becomes

$$C_{\underline{K}} = C_{N_1 N_2 N_3} = \frac{2\pi}{L^3} \left[ \frac{2}{k^2 + \beta^2} - \frac{1}{k^2} + (-1)^{N_1 + N_2 + N_3} \left( \frac{4.7}{k^2 + 2} + \frac{1}{k^2} \right) \right] \quad (5-17)$$

where  $k^2 = \frac{\pi^2}{L^2} (N_1^2 + N_2^2 + N_3^2)$

## Results

The evaluation of the matrix elements <sup>of (5-15)</sup> and the diagonalization of the matrix were done on the I.B.M. 1620 computer. The ground state energy of a positron in the crystal, estimated as an upper bound, was found to be -3.99 e.v. after correction due to shift of origin of the crystal potential.

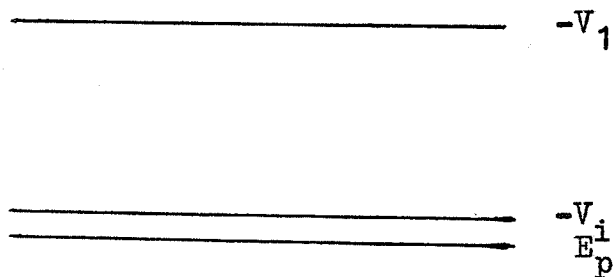
## CHAPTER SIX

### DISCUSSION AND CONCLUSIONS

We will now discuss the possibility of positronium formation and persistence in the crystal. Let  $E_p$  be the ground state energy of ~~e-bound~~ positronium in the crystal. We have obtained a value of -17.54 e.v. for it, which is not affected by any shift of origin of the crystal potential. Let  $E^+$  be the actual energy of the positron, and  $E_0^+$ , the energy of its ground state,  $-V_i$ , the energy of an electron at the top of the valence band, and  $-V_1$ , the energy of an electron at the bottom of the conduction band. The values of  $E_0^+$ ,  $V_i$ , and  $V_1$  were obtained as -3.99 e.v., 17.03 e.v., and 8.14 e.v. respectively.

A positron will be able to capture an electron at the top of the valence band and form positronium if the following inequality is satisfied:

$$E^+ - V_i > E_p \quad (6-1)$$



Energy level diagram

The positronium so formed will be stable against decomposition into a positron in the ground state and an electron deposited at the bottom of the conduction band provided

$$E^+ - V_i < E_0^+ - V_1 \quad (6-2)$$

The Ore gap, if it exists, will cover the range

$$(E_p + V_i) \text{ to } (E_0^+ + V_i - V_1) \text{ if } E_0^+ < E_p + V_i \quad (6-3)$$

or 
$$E_0^+ \text{ to } (E_0^+ + V_i - V_1) \text{ if } E_0^+ > E_p + V_i \quad (6-4)$$

With the values obtained for these quantities,

$$E_0^+ < E_p + V_i$$

Therefore, an Ore gap of a range from -0.51 e.v. to + 4.90 e.v. as given by (6-3) exists, giving a gap of 5.41 e.v.

We have, however, completely neglected the polarization effect of a positron in the crystal, which distorts the distribution of electrons on its passage through the crystal, and tends to draw electrons close to it. If we take the free positronium binding energy of 6.8 e.v., which is in fact far too much, as a correction for polarization, we get a value of -10.79 e.v. for  $E_0^+$  and we get no Ore gap. Because of the various approximations introduced in the calculations in this thesis, with an Ore gap of 1 or 2 e.v. we cannot positively draw any conclusions as to whether positronium will form and persist. We can, however, say this much: there is an Ore

gap for positronium formation and persistence in lithium fluoride provided the polarization effect of the positron is very much smaller than 5 e.v. This, we would guess, is likely to be the case; for, while the effect of a tendency for the electron density to be increased in the neighbourhood of the positron would result in a decrease in energy, this would, at least in part, be offset by an increase in energy due to the displacement of the electrons from their normal locations in the crystal. We would expect the polarization effect to be a second order effect that would lower the positron energy by an amount much less than the binding energy of free positronium.

One last remark we would like to make is that in the fitting of a Coulomb-plus-Yukawa curve to the potential due to a fluorine ion, it was found that owing to the logarithmic nature of the graph, a small deviation of the straight line yields a different intercept so that the constant  $c$  in the Yukawa term can lie in the range from 4.5 to 4.9. It was found, however, that  $E_p$ ,  $E_0^+$  and  $V_1$  are not very sensitive to the change in  $c$ , and even more insensitive to the change in  $\beta$ , while  $V_1$  is extremely sensitive to the change in  $c$ . The energy gap for  $c = 4.7$ , however, is of the right order

as is obtainable by extrapolating the experimental data of the energy gaps of other alkali halides.<sup>A(4)</sup> Hence, the results obtained in the present thesis may be regarded as acceptable.

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APPENDIX ONE — A(1)

To prove the expression for  $d\tau$  in (2-6)

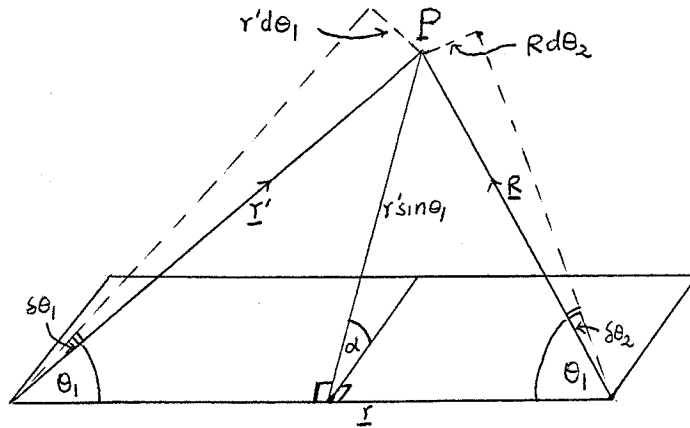


fig. 5

With reference to fig. 5,  $\alpha$  is the angle of rotation of the plane formed by  $\underline{r}'$  and  $\underline{R}$  about the axis  $\underline{r}$ . If  $\alpha$  and  $\underline{r}'$  are kept fixed,  $R$  can be varied by rotation of  $\underline{r}'$  through an arc of  $r'd\theta_1$ . Similarly, for fixed  $\alpha$  and  $R$ ,  $\underline{r}'$  can be varied by rotation of  $R$  through an arc of  $Rd\theta_2$ . For fixed  $\underline{r}'$  and  $R$ ,  $\alpha$  is varied when the point  $P$  traces an arc  $r'sine_1 d\alpha$ , perpendicular to the other two arcs which make an angle  $\pi - \theta_3$ . Hence

$$d\tau = r'd\theta_1 R d\theta_2 \sin\theta_3 r' \sin\theta_1 d\alpha$$

Now  $R^2 = r'^2 + r^2 - 2r'r\cos\theta_1$

$$(R + dR)^2 = r'^2 + r^2 - 2r'r\cos(\theta_1 + d\theta_1)$$

$$\therefore RdR = rr' \sin\theta_1 d\theta_1$$

Similarly  $r'dr' = rR \sin\theta_2 d\theta_2$

Also  $\frac{\sin\theta_3}{\sin\theta_2} = \frac{r}{r'}$ ,  $\therefore d\tau = \frac{r'R}{r} dr' dR d\alpha$  q. e. d.

APPENDIX TWO — A(2)

To find the Fourier coefficients of the crystal potential  $V(\underline{R})$

Since  $V(\underline{R}) = V(-\underline{R})$ ,

$$\begin{aligned}
 C_{\underline{K}} &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\underline{V}_R} e^{2\pi i \underline{K} \cdot \underline{R}} V(\underline{R}) d\underline{r}_R \\
 &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\underline{V}_R} e^{-2\pi i \underline{K} \cdot \underline{R}} V(-\underline{R}) d\underline{r}_R \\
 &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\underline{V}_R} e^{-2\pi i \underline{K} \cdot \underline{R}} V(\underline{R}) d\underline{r}_R \\
 &= C_{-\underline{K}} \\
 &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\underline{V}_R} e^{-2\pi i \underline{K} \cdot \underline{R}} \sum_j \left[ v_1(\underline{R}-\underline{R}_j) + v_2(\underline{R}-\underline{R}_j-\underline{a}) \right] d\underline{r}_R \\
 &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\underline{V}_R} e^{-2\pi i \underline{K} \cdot \underline{R}} \sum_j \left[ \frac{1}{|\underline{R}-\underline{R}_j|} + \frac{2e^{-\alpha|\underline{R}-\underline{R}_j|}}{|\underline{R}-\underline{R}_j|} \right. \\
 &\quad \left. - \frac{1}{|\underline{R}-\underline{R}_j-\underline{a}|} + \frac{4.7e^{-\beta|\underline{R}-\underline{R}_j-\underline{a}|}}{|\underline{R}-\underline{R}_j-\underline{a}|} \right] d\underline{r}_R
 \end{aligned}$$

Now

$$\begin{aligned}
 &\int_{\underline{V}_R} \frac{e^{-\alpha|\underline{R}-\underline{R}_j|}}{|\underline{R}-\underline{R}_j|} e^{-2\pi i \underline{K} \cdot \underline{R}} d\underline{r}_R \\
 &= \int_{\underline{V}_R} \frac{e^{-\alpha \underline{R}}}{\underline{R}} e^{-2\pi i \underline{K} \cdot (\underline{R} + \underline{R}_j)} d\underline{r}_R \quad \text{by a shift of origin} \\
 &= \int_{\underline{V}_R} \frac{e^{-\alpha \underline{R}}}{\underline{R}} e^{-2\pi i \underline{K} \cdot \underline{R}} d\underline{r}_R \quad \text{because } \underline{K} \text{ is a vector of the} \\
 &\quad \text{reciprocal lattice.}
 \end{aligned}$$

$$\frac{e^{-\beta |\underline{R}-\underline{R}_j-\underline{a}|}}{|\underline{R}-\underline{R}_j-\underline{a}|} e^{-2\pi i \underline{K} \cdot \underline{R}} d\underline{r}_R$$

$$= \int_{\underline{r}_R} \frac{e^{-\beta R}}{R} e^{-2\pi i \underline{K} \cdot \underline{R}} e^{-2\pi i \underline{K} \cdot \underline{a}} d\underline{r}_R \quad \text{by a shift of origin}$$

The other terms will be obtained by putting  $\alpha$  or  $\beta$  zero. All these expressions are independent of  $R_j$ . In the summation, the number of  $R_j$  is  $S^3/2L^3$ , since  $2L^3$  is the volume of a unit cell, and since to each unit cell in space there corresponds one vector  $\underline{R}_j$ .

$$\therefore C_{\underline{K}} = \frac{1}{2L^3} \int_{\underline{r}_R} e^{-2\pi i \underline{K} \cdot \underline{R}} \left[ \frac{1}{R} + \frac{2e^{-\alpha R}}{R} - \frac{e^{-2\pi i \underline{K} \cdot \underline{a}}}{R} + \frac{4.7e^{-\beta R}}{R} e^{-2\pi i \underline{K} \cdot \underline{a}} \right] d\underline{r}_R$$

Now

$$\int_{\underline{r}_R} \frac{e^{-\alpha R} e^{-2\pi i \underline{K} \cdot \underline{R}}}{R} d\underline{r}_R$$

$$= \int_{\underline{r}_R} \frac{e^{-\alpha R} e^{-2\pi i KR \cos \theta}}{R} R^2 dR \sin \theta d\theta d\varphi$$

$$= \frac{4\pi}{4\pi^2 K^2 + \alpha^2}$$

$$\therefore \int_{\underline{r}_R} \frac{e^{-2\pi i \underline{K} \cdot \underline{R}}}{R} d\underline{r}_R = \lim_{\alpha \rightarrow 0} \frac{4\pi}{4\pi^2 K^2 + \alpha^2} = \frac{4\pi}{4\pi^2 K^2}$$

$$\therefore C_{\underline{K}} = \frac{2\pi}{L^3} \left[ \frac{2}{4\pi^2 K^2 + \alpha^2} + \frac{1}{4\pi^2 K^2} + e^{-2\pi i \underline{K} \cdot \underline{a}} \left( \frac{4.7}{4\pi^2 K^2 + \beta^2} - \frac{1}{4\pi^2 K^2} \right) \right]$$

It is obvious that the value of  $C_{\underline{K}}$  should be independent of the choice of  $\underline{a}$ , which is the position vector of any negative ion with respect to ~~the origin.~~ <sup>any positive ion.</sup> With reference to fig. 2, p. 26, one value of  $\underline{a}$  would be

$$\underline{a} = \frac{1}{2}(\underline{a}_1 + \underline{a}_2 + \underline{a}_3)$$

A general value of  $\underline{a}$  would be  $\underline{a} + \underline{R}_j$ , where  $\underline{R}_j$  is the position vector of any positive ion, and

$$\underline{R}_j = m_1 \underline{a}_1 + m_2 \underline{a}_2 + m_3 \underline{a}_3,$$

where  $m_1$ ,  $m_2$  and  $m_3$  are integers.

$$\therefore \underline{a} = (m_1 + \frac{1}{2})\underline{a}_1 + (m_2 + \frac{1}{2})\underline{a}_2 + (m_3 + \frac{1}{2})\underline{a}_3$$

is a general value of  $\underline{a}$ .

The three basic reciprocal lattice vectors are

$$\underline{b}_1 = \frac{\underline{a}_2 \wedge \underline{a}_3}{\underline{a}_1 \cdot \underline{a}_2 \wedge \underline{a}_3} \quad \text{etc.}$$

$$\therefore \underline{a}_i \cdot \underline{b}_j = \delta_{i,j}$$

Now  $\underline{K}$  is a vector of the reciprocal lattice.

$$\therefore \underline{K} = n_1 \underline{b}_1 + n_2 \underline{b}_2 + n_3 \underline{b}_3, \quad \text{where } n_1, n_2, n_3 \text{ are integers.}$$

Write  $\underline{k} = 2\pi \underline{K}$

$$\begin{aligned}\therefore e^{-2\pi i \underline{K} \cdot \underline{a}} &= e^{-2\pi i \left[ n_1(m_1 + \frac{1}{2}) + n_2(m_2 + \frac{1}{2}) + n_3(m_3 + \frac{1}{2}) \right]} \\ &= (-1)^{n_1+n_2+n_3}\end{aligned}$$

$$\therefore C_{\underline{K}} = C_{n_1 n_2 n_3}$$

$$= \frac{2\pi}{L^3} \left[ \frac{2}{k^2 + \alpha^2} + \frac{1}{k^2} + (-1)^{n_1+n_2+n_3} \left( \frac{4.7}{k^2 + \beta^2} - \frac{1}{k^2} \right) \right]$$

where

$$k^2 = \frac{\pi^2}{L^2} \left[ (n_2 + n_3 - n_1)^2 + (n_3 + n_1 - n_2)^2 + (n_1 + n_2 - n_3)^2 \right]$$

APPENDIX THREE — A(3)

Expressions for evaluation of an upper bound to the ground state energy of positronium in a lithium fluoride crystal

With notations as introduced in chapter 3, the second order wavefunction is

$$\psi = \psi_{0,100} + \sum_{\substack{k,nlm \\ k \neq 0}} \frac{(\psi_{0,100} | H_1 | \psi_{k,nlm})}{E_1 - E_n - \frac{1}{4}k^2} \psi_{k,nlm}$$

Denote 
$$\psi' = \sum_{\substack{k,nlm \\ k \neq 0}} \frac{(\psi_{0,100} | H_1 | \psi_{k,nlm})}{E_1 - E_n - \frac{1}{4}k^2} \psi_{k,nlm}$$

and 
$$\psi_0 = \psi_{0,100}$$

$$\begin{aligned} (\psi | H | \psi) &= (\psi_0 | H_0 | \psi_0) + 2(\psi_0 | H_0 | \psi') + (\psi' | H_0 | \psi') \\ &\quad + (\psi_0 | H_1 | \psi_0) + 2(\psi_0 | H_1 | \psi') + (\psi' | H_1 | \psi') \end{aligned}$$

$$(\psi_0 | H_0 | \psi_0) = E_1$$

$$(\psi_0 | H_0 | \psi') = 0 \quad \text{because } \psi' \text{ and } \psi_0 \text{ are orthogonal.}$$

$$(\psi' | H_0 | \psi') = \sum_{\substack{k,nlm \\ k \neq 0}} \frac{(E_1 + \frac{1}{4}k^2) |(\psi_{0,100} | H_1 | \psi_{k,nlm})|^2}{(E_1 - E_n - \frac{1}{4}k^2)^2}$$

$$(\psi_0 | H_1 | \psi_0) = 0 \quad \text{from parity considerations.}$$

$$(\psi_0 | H_1 | \psi') = \sum_{\substack{k,nlm \\ k \neq 0}} \frac{|(\psi_{0,100} | H_1 | \psi_{k,nlm})|^2}{E_1 - E_n - \frac{1}{4}k^2}$$

$$(\psi' | H_1 | \psi') = \sum_{\substack{k,nlm \\ k;n'l'm'}} (\psi_{k,nlm} | H_1 | \psi_{0,100}) (\psi_{0,100} | H_1 | \psi_{k,n'l'm'}) (\psi_{k,nlm} | H_1 | \psi_{k,n'l'm'}) = 0$$

from parity considerations.

$$\begin{aligned} \therefore (\psi | H | \psi) &= E_1 + 2 \sum_{k, nlm} \frac{|(\psi_{0,100} | H_1 | \psi_{k,nlm})|^2}{(E_1 - E_n - \frac{1}{4}k^2)} \\ &+ \sum_{k, nlm} \frac{(E_n + \frac{1}{4}k^2) |(\psi_{0,100} | H_1 | \psi_{k,nlm})|^2}{(E_1 - E_n - \frac{1}{4}k^2)^2} \end{aligned}$$

$$(\psi | \psi) = (\psi_0 | \psi_0) + (\psi' | \psi')$$

$$= 1 + \sum_{k, nlm} \frac{|(\psi_{0,100} | H_1 | \psi_{k,nlm})|^2}{(E_1 - E_n - \frac{1}{4}k^2)^2}$$

Now  $(\psi_{0,100} | H_1 | \psi_{k,nlm})$

$$\begin{aligned} &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\underline{r}_R, \underline{r}_r} \phi_{100}^*(\underline{r}) \left[ V(\underline{R} - \frac{\underline{r}}{2}) - V(\underline{R} + \frac{\underline{r}}{2}) \right] \phi_{nlm}(\underline{r}) e^{i\mathbf{k} \cdot \underline{r}} d\underline{r}_R d\underline{r}_r \\ &= \lim_{S \rightarrow \infty} \frac{1}{S^3} \int_{\underline{r}_R} e^{i\mathbf{k} \cdot \underline{R}} V(\underline{R}) d\underline{r}_R \int_{\underline{r}_r} \phi_{100}^*(\underline{r}) \phi_{nlm}(\underline{r}) \left[ e^{i\mathbf{k} \cdot \frac{\underline{r}}{2}} - e^{-i\mathbf{k} \cdot \frac{\underline{r}}{2}} \right] d\underline{r}_r \\ &= 2iC_{\underline{K}} \int \phi_{100}^*(\underline{r}) \phi_{nlm}(\underline{r}) \sin(\frac{\mathbf{k} \cdot \underline{r}}{2}) d\underline{r}_r \quad \text{by a suitable shift} \\ &\hspace{15em} \text{of origin} \end{aligned}$$

$$\therefore |(\psi_{0,100} | H_1 | \psi_{k,nlm})|^2 = 4 |C_{\underline{K}}|^2 \left| \int \phi_{100}^*(\underline{r}) \cdot \phi_{nlm}(\underline{r}) \sin(\frac{\mathbf{k} \cdot \underline{r}}{2}) d\underline{r}_r \right|^2$$

Since  $E_n$  vanishes as  $1/n^2$ , as an approximation, we can

neglect  $E_n$  and then make a correction for it afterwards.

We express  $\sin(\frac{\mathbf{k} \cdot \mathbf{r}}{2})$  in terms of  $e^{i\mathbf{k} \cdot \mathbf{r}}$  and make use of the following relations:

$$e^{i\mathbf{k} \cdot \mathbf{r}} = \sum_{l=0}^{\infty} (2l+1) i^l P_l(\cos \theta) j_l(kr)$$

$$\phi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_l^m(\theta, \varphi)$$

$$\sum_{nlm} \phi_{nlm}^*(\mathbf{r}) \phi_{nlm}(\mathbf{r}) = \delta(\mathbf{r}' - \mathbf{r})$$

where  $P_l(\cos \theta)$  is a Legendre Polynomial of degree  $l$ ,  $j_l(kr)$  is a spherical Bessel function of degree  $l$ ,  $R_{nl}(r)$  is the normalized radial part of  $\phi_{nlm}(\mathbf{r})$  and  $Y_l^m(\theta, \varphi)$  is the spherical part of it.

Putting these into the expressions for  $(\psi | \psi)$  and  $(\psi | H | \psi)$ , we obtain (3-7) and (3-8).



APPENDIX FOUR — A(4)

Electron energy gap for the lithium fluoride crystal by graphical extrapolation method from experimental results of other alkali halides.<sup>R(6)</sup>

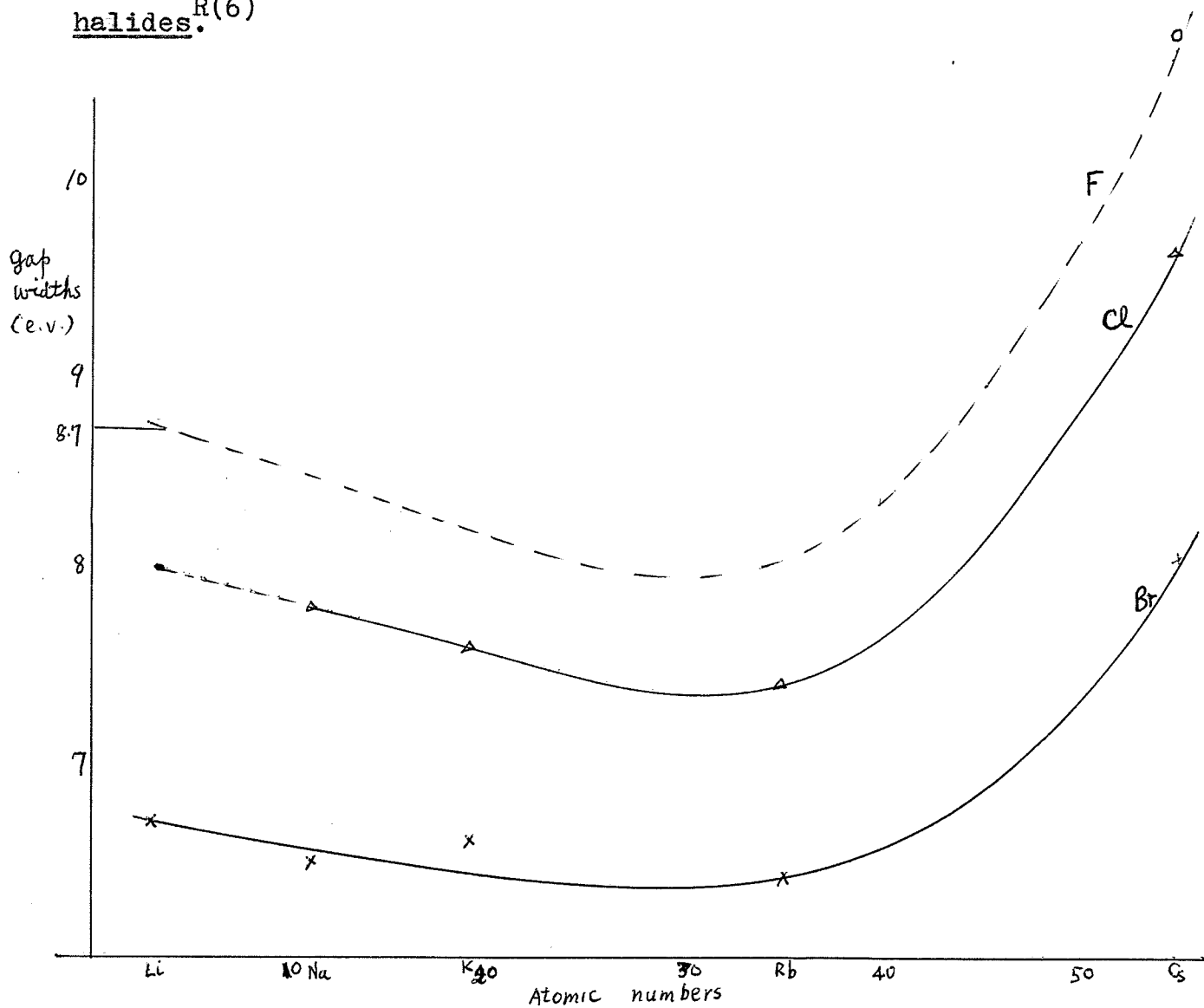


fig. 6

Gap widths plotted against atomic numbers of alkali metals

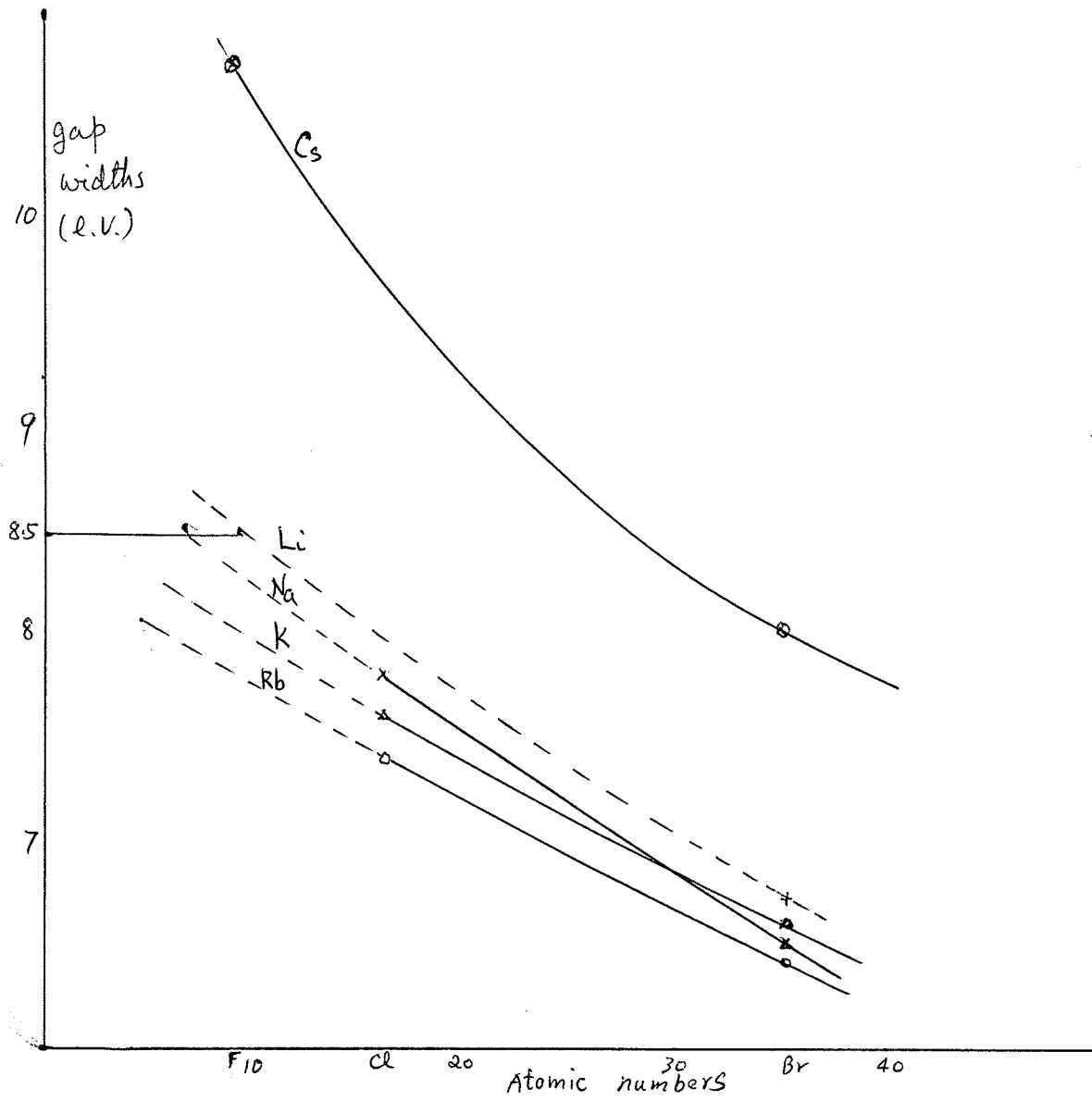


fig. 7

Gap widths plotted against atomic numbers of halogens

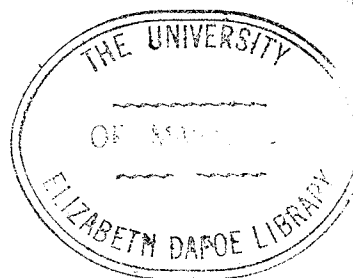
SUPPLEMENT

POSITRONIUM IN LITHIUM FLUORIDE

— E. Tong —

1963-1964

A thesis submitted to the Faculty of Graduate Studies at the University of Manitoba in partial fulfilment of the requirements for the degree of Master of Science.



SUPPLEMENT TO THE THESIS

I.B.M. MACHINE PROGRAMMES

(1) CURVE-FITTING : EQUATION (2-9)

```
A=7.234
B=0.31
C=2.37
D=0.85
2 FORMAT (4H R= E10.2,10X10H LOG(RV)= E10.5)
DO1 I=1,7
R=I
U=2.*C*R
X=((3.*A*A)/(2.*C*C))*EXP(-U)
Y=R*R+3.*R/C+9./(2.*C*C)+3./(C*C*C*R)
V=2.*D*R
E=((3.*B*B)/(2.*D*D))*EXP(-V)
F=R*R+3.*R/D+9./(2.*D*D)+3./(D*D*D*R)
W=(C+D)*R
P=((12.*A*B)/((C+D)**2.))*EXP(-W)
Q=R*R+(6.*R)/(C+D)+18./((C+D)**2.)+24./(R*(C+D)**3.)
S=X*Y+E*F+P*Q
G=R*S
H=LOG(G)
1 PRINT 2,R,H
PAUSE
END
```

(2) GROUND STATE ENERGY OF POSITRONIUM IN LIF : EQUATION (3-6)

```
1 FORMAT (I3)
2 FORMAT (F9.5)
  DIMENSION E(5),B(4),S(4,2),P(5),Q(5),U(2),T(2),ENG(2)
3 DO 4 I=1,4
  P(1)=0.0
  DO 4 J=1,2
4 S(I,J)=0.0
  ALPHA=(4.152*0.5292)**2.
  BETA=1.27*1.27
  XL=3.78
  WC=0.5
  E(1)=-0.5
  E(2)=-0.125
  E(3)=-0.5/9.
  E(4)=-0.5/16.
  E(5)=-0.5/25.
  ACCEPT1,NI
  QI=NI
  XK=-QI
  XJ=0.0
  XI=1.0
7 IF(XI-XJ)15,15,8
8 IF(XI-XK)15,15,9
9 IF(XJ-XK)16,16,10
10 A=3.*(XI*XI+XJ*XJ+XK*XK)-2.*(XI*XJ+XJ*XK+XK*XI)
  C2=(A*3.14159*3.14159)/(XL*XL)
  C1=SQRT(C2)
  C3=C1*C2
  C5=C3*C2
  C7=C5*C2
  Y21=384.*C1/((4.*C2+9.))**3.)
  Y21S=Y21*Y21/6.
  Y31=3.55555*C3+2.10699*C1
  Y31=Y31/((1.77778+C2)**4.)
  Y31S=Y31*Y31/6.
  Y41=1.831055*C1+5.15626*C3+3.75*C5
  Y41=Y41/((1.5625+C2)**5.)
  Y41S=Y41*Y41/15.
  Y43=0.625*C3/((1.5625+C2)**5.)
  Y43S=Y43*Y43/35.
  Y51=1.69869*C1+6.54704*C3+8.6016*C5+3.84*C7
  Y51=Y51/((1.44+C2)**6.)
  Y51S=Y51*Y51/30.
```

```

Y53=(0.707789*C3+0.8192*C5)/((1.44+C2)**6.)
Y53S=Y53*Y53/70.
R=1./(E(1)-WC*C2)
DO40 I=2,5
40 P(I)=1./(E(1)-E(I)-WC*C2)
DO41 J=2,5
41 Q(J)=2.*(P(J)-R)+(E(J)+WC*C2)*P(J)*P(J)-(WC*C2*R*R)
Z1=(1.-1./((1.+C2)**2.))* (4.*R+2.*WC*C2*R*R)
Z2=48.*Y21S*Q(2)
Z3=48.*Y31S*Q(3)
Z4=((48.*Y41S)+(112.*Y43S))*Q(4)
Z5=((48.*Y51S)+(112.*Y53S))*Q(5)
D1=2.*(1.-1./((1.+C2)**2.))*R*R
D2=48.*Y21S*(P(2)*P(2)-R*R)
D3=48.*Y31S*(P(3)*P(3)-R*R)
D4=((48.*Y41S)+(112.*Y43S))* (P(4)*P(4)-R*R)
D5=((48.*Y51S)+(112.*Y53S))* (P(5)*P(5)-R*R)
ENG(1)=Z1+Z2+Z3+Z4+Z5
ENG(2)=D1+D2+D3+D4+D5
B(1)=2./(C2+ALPHA)
B(2)=4.7/(C2+BETA)
N=ABS(XI+XJ+XK)
IF(N-(N/2)*2)30,30,31
30 B(4)=B(1)+B(2)
GO TO 32
31 B(4)=B(1)-B(2)+2./C2
32 B(3)=4.*3.14159*B(4)/(XL*XL*XL)
T(1)=ENG(1)*B(3)*B(3)
T(2)=ENG(2)*B(3)*B(3)
IF(XJ-XK)24,24,12
12 IF(XJ)13,13,14
13 S(1,1)=S(1,1)+6.*T(1)
S(1,2)=S(1,2)+6.*T(2)
GO TO 15
14 S(2,1)=S(2,1)+12.*T(1)
S(2,2)=S(2,2)+12.*T(2)
15 XI=XI+1.
IF(XI-QI)7,7,16
16 XJ=XJ+1.
XI=XJ+1.
IF(XI-QI)7,7,17
17 XK=XK+1.
IF(XK)19,18,18
18 XJ=XK+1.
GO TO 20

```

```

19 XJ=0.0
20 XI=XJ+1.
   IF(XI-QI)7,7,21
21 XJ=-QI
   XK=-QI
   XI=-QI
   GO TO 10
22 XI=XI+1.
   IF(XI-QI)10,10,23
23 XJ=XJ+1.
   XK=XJ
   XI=XJ
   IF(XI-QI)10,10,27
24 IF(XI-XJ)25,25,26
25 S(3,1)=S(3,1)+T(1)
   S(3,2)=S(3,2)+T(2)
   GO TO 22
26 S(4,1)=S(4,1)+6.*T(1)
   S(4,2)=S(4,2)+6.*T(2)
   GO TO 22
27 U(1)=S(1,1)+S(2,1)+S(3,1)+S(4,1)
   U(2)=S(1,2)+S(2,2)+S(3,2)+S(4,2)
   SS=(E(1)+U(1))/(1.+U(2))
   PRINT2,SS
   GO TO 3
END

```

(3a) FOURIER COEFFICIENTS OF THE CRYSTAL POTENTIAL FOR AN

ELECTRON IN LIF : EQUATION (4-42)

```
1 FORMAT (I2,I2,I2,E12.8)
  DIMENSION B(4)
  ALPHA=(4.152*0.5292)**2.
  BETA=1.27*1.27
  XL=3.78
  XK=9.0
  XJ=9.0
  XI=9.0
7  A=XI*XI+XJ*XJ+XK*XK
  C=(A*3.14159*3.14159)/(XL*XL)
  B(1)=2./(C+ALPHA)
  B(2)=4.7/(C+BETA)
  N=XI+XJ+XK
  IF(N-(N/2)*2)8,8,9
8  B(4)=B(1)+B(2)
  GO TO 10
9  B(4)=B(1)-B(2)+2./C
10 B(3)=4.*3.14159*B(4)/(XL*XL*XL)
  I=XI
  J=XJ
  K=XK
  IJ=I+J
  JK=J+K
  IF(IJ-(IJ/2)*2)2,2,3
2  IF(JK-(JK/2)*2)4,4,3
4  PUNCH1,I,J,K,B(3)
3  XK=K-1
  IF(XK)16,7,7
16 XJ=J-1
  XK=XJ
  IF(XJ)17,7,7
17 XI=I-1
  XJ=XI
  XK=XI
  IF(XI)18,7,7
18 PAUSE
  END
```



(3b) TO FIND THE ELECTRON ENERGY AT THE FIRST BRILLOUIN ZONE  
BOUNDARY IN LIF, MATRIX ELEMENTS GIVEN BY EQUATION (4-44)  
ARE COMPUTED FOR  $\Psi_1$ .

```

9 FORMAT (I2,I2,I2,E12.8)
1 FORMAT (F4.1,F4.1,F4.1,F4.1,F4.1,F4.1,E14.8)
  DIMENSION X(3),Y(3),B(3),F(3),D(3),A(3),C(10,10,10)
  WC=3.14159*3.14159/((3.78)**2.)
3 READ9,I,J,K,G
  I=I+1
  J=J+1
  K=K+1
  C(I,J,K)=G
  IF(K-1)130,130,3
130 IF(J-1)131,131,3
131 IF(I-1)132,132,3
132 CONTINUE
  X(1)=4.5
  X(2)=4.5
  X(3)=4.5
  Y(1)=4.5
  Y(2)=4.5
  Y(3)=4.5
7 P=0.0
  Q=0.0
  T=0.0
  DO 110 I=1,3
  B(I)=Y(1)
  D(I)=X(1)
  DO 109 J=2,3
  IF(I-2)5,8,12
5 IF(J-3)23,60,60
8 IF(J-3)60,61,61
12 IF(J-3)61,62,62
23 B(J+1)=Y(2)
  B(2)=Y(3)
  D(J+1)=X(2)
  D(2)=X(3)
  GO TO 33
60 B(J-1)=Y(2)
  B(3)=Y(3)
  D(J-1)=X(2)

```

```

D(3)=X(3)
GO TO 33
61 B(J)=Y(2)
   B(1)=Y(3)
   D(J)=X(2)
   D(1)=X(3)
   GO TO 33
62 B(J-1)=Y(3)
   B(1)=Y(2)
   D(J-1)=X(3)
   D(1)=X(2)
33 CONTINUE
DO 108 NI=1,3,2
HI=NI
F(1)=2.*B(1)-HI*B(1)
A(1)=2.*D(1)-HI*D(1)
DO 107 NJ=1,3,2
HJ=NJ
F(2)=2.*B(2)-HJ*B(2)
A(2)=2.*D(2)-HJ*D(2)
DO 106 NK=1,3,2
HK=NK
F(3)=2.*B(3)-HK*B(3)
A(3)=2.*D(3)-HK*D(3)
IF(Y(1)-F(1))203,200,203
200 IF(Y(2)-F(2))203,201,203
201 IF(Y(3)-F(3))203,202,203
202 Q=Q+1.0
203 IF(X(1)-A(1))208,205,208
205 IF(X(2)-A(2))208,206,208
206 IF(X(3)-A(3))208,207,208
207 T=T+1.0
208 ZI=ABSF(X(1)-F(1))
   ZJ=ABSF(X(2)-F(2))
   ZK=ABSF(X(3)-F(3))
   IZJ=ZI+ZJ
   IZK=ZI+ZK
   IF(IZJ-(IZJ/2)*2)120,120,106
120 IF(IZK-(IZK/2)*2)119,119,106
119 IF(ZI-ZJ)13,14,14
   14 IF(ZJ-ZK)15,16,16
   15 IF(ZI-ZK)17,18,18
   13 IF(ZK-ZJ)19,20,20
   19 IF(ZI-ZK)21,22,22
20 L=ZK

```

```

M=ZJ
N=ZI
GO TO 11
21 L=ZJ
M=ZK
N=ZI
GO TO 11
22 L=ZJ
M=ZI
N=ZK
GO TO 11
16 L=ZI
M=ZJ
N=ZK
GO TO 11
18 L=ZI
M=ZK
N=ZJ
GO TO 11
17 L=ZK
M=ZI
N=ZJ
11 L=L+1
M=M+1
N=N+1
P=P-C(L,M,N)
106 CONTINUE
107 CONTINUE
108 CONTINUE
109 CONTINUE
110 CONTINUE
QN=SQRTF(Q)
TN=SQRTF(T)
P=P/(QN*TN)
IF(X(1)-Y(1))91,90,91
90 IF(X(2)-Y(2))91,92,91
92 IF(X(3)-Y(3))91,93,91
93 P=P+(X(1)*X(1)+X(2)*X(2)+X(3)*X(3))*WC
91 PUNCH1,X(1),X(2),X(3),Y(1),Y(2),Y(3),P
Y(3)=Y(3)-1.0
IF(Y(3)-0.5)24,7,7
24 Y(2)=Y(2)-1.0
Y(3)=Y(2)
IF(Y(2)-0.5)25,7,7
25 Y(1)=Y(1)-1.0

```

```
Y(2)=Y(1)
Y(3)=Y(1)
IF(Y(1)-0.5)26,7,7
26 X(3)=X(3)-1.0
IF(X(3)-0.5)27,2,2
2 Y(1)=X(1)
Y(2)=X(2)
Y(3)=X(3)
GO TO 7
27 X(2)=X(2)-1.0
X(3)=X(2)
IF(X(2)-0.5)28,2,2
28 X(1)=X(1)-1.0
X(2)=X(1)
X(3)=X(1)
IF(X(1)-0.5)29,2,2
29 PAUSE
END
```

(3c) MATRIX ELEMENTS GIVEN BY EQUATION (4-44) COMPUTED FOR  $\Psi_3$ .

The logic used is the same as that in (3b). The first change comes after statement 33:

```
33 CONTINUE
   DO 108 NI=1,3,2
   IF(NI-1)51,51,52
51 GI=1.0
   GO TO 71
52 GI=-1.0
71 HI=NI
   F(1)=2.*B(1)-HI*B(1)
   A(1)=2.*D(1)-HI*D(1)
   DO 107 NJ=1,3,2
   IF(NJ-1)53,53,54
53 GJ=1.0
   GO TO 72
54 GJ=-1.0
72 HJ=NJ
   F(2)=2.*B(2)-HJ*B(2)
   A(2)=2.*D(2)-HJ*D(2)
   DO 106 NK=1,3,2
   IF(NK-1)55,55,56
55 GK=1.0
   GO TO 73
56 GK=-1.0
73 HK=NK
   F(3)=2.*B(3)-HK*B(3)
   A(3)=2.*D(3)-HK*D(3)
   GIJK=GI*GJ*GK
   IF(X(1)-A(1))203,205,203
205 IF(X(2)-A(2))203,206,203
206 IF(X(3)-A(3))203,207,203
207 T=T+GIJK
203 IF(Y(1)-F(1))208,200,208
200 IF(Y(2)-F(2))208,201,208
201 IF(Y(3)-F(3))208,202,208
202 Q=Q+GIJK
208 ZI=ABSF(X(1)-F(1))
```

The second change comes after statement 11 :

```

11 L=L+1
   M=M+1
   N=N+1
   P=P-G.IJK*C(L,M,N)
106 CONTINUE
107 CONTINUE
108 CONTINUE
109 CONTINUE
110 CONTINUE
   IF(T)26,26,301
301 IF(Q)303,303,304
304 TN=SQRTF(T)
   QN=SQRTF(Q)
   P=P/(QN*TN)
   IF(X(1)-Y(1))91,90,91
90 IF(X(2)-Y(2))91,92,91
92 IF(X(3)-Y(3))91,93,91
93 P=P+(X(1)*X(1)+X(2)*X(2)+ X(3)*X(3))*WC
91 PUNCH1,X(1),X(2),X(3),Y(1),Y(2),Y(3),P
303 Y(3)=Y(3)-1.0

```

The rest of the programme is identical with that of (3b)

(4a) FOURIER COEFFICIENTS OF THE CRYSTAL POTENTIAL FOR A  
POSITRON IN LIF : EQUATION (5-17)

The logic and programming here is identical with that of (3a) except that statement 9 is changed to

$$9 \quad B(4)=B(2)-B(1)-2./C$$

(4b) POSITRON GROUND STATE ENERGY IN LIF. COMPUTATION OF MATRIX  
ELEMENTS GIVEN BY EQUATION (5-15)

The logic and programming is identical with that of (3b). The only changes take place after statement 91:

```
91 PUNCH1,X(1),X(2),X(3),Y(1),Y(2),Y(3),P
    Y(3)=Y(3)-2.0
    IF(Y(3))24,7,7
24 Y(2)=Y(2)-2.0
    Y(3)=Y(2)
    IF(Y(2))25,7,7
25 Y(1)=Y(1)-1.0
    Y(2)=Y(1)
    Y(3)=Y(1)
    IF(Y(1))26,7,7
26 X(3)=X(3)-2.0
    IF(X(3))27,2,2
    2 Y(1)=X(1)
    Y(2)=X(2)
    Y(3)=X(3)
    GO TO 7
27 X(2)=X(2)-2.0
    X(3)=X(2)
    IF(X(2))28,2,2
28 X(1)=X(1)-1.0
    X(2)=X(1)
    X(3)=X(1)
    IF(X(1))29,2,2
29 PAUSE
    END
```

(5) CONVERSION OF DATA IN FORMAT E12.8 TO THE SPECIALLY  
NORMALIZED FORMAT USED IN THE PROGRAM FOR DIAGONALIZING A  
SYMMETRIC MATRIX.

```
      DIMENSION NAR(11)
100  FORMAT (11A1)
      READ 100 (NAR(I), I=1,11)
101  FORMAT (4I1,I2,I7,2A1)
      NROW=1
      NCOL=1
      NEX=44
      P1=ABS(P*1000000.)
   9  IF(1.-P1)10,10,12
  10  NEX=NEX+1
      P1=P1/10.0
      GO TO 9
  12  NP=P*100000000.
      NROW1=NROW/10
      NROW2=NROW-(NROW/10)*10
      NCOL1=NCOL/10
      NCOL2=NCOL-(NCOL/10)*10
      IF(NCOL-N)15,13,15
  13  NROW=NROW+1
      NCOL=NROW
  15  NP2=NP-(NP/10)*10
      NP1=NP/10
      IF(NP2)17,18,28
  17  NP2=ABS(NP2)
      NP2=NAR(NP2)
      GO TO 28
  18  NP2=NAR(10)
  28  PUNCH 101 (NROW1,NROW2,NCOL1,NCOL,NEX,NP1,NP2,NAR(11))
      PAUSE
      END
```

The 11 NAR(I) are J,K,L,M,N,O,P,Q,R, $\bar{O}$ , $\ddagger$ .

✱ obtainable from I.B.M.