THE ACTIVATION ENERGY FOR F-CENTRE STEP DIFFUSION
AND
F-CENTRE ABSORPTION AND EMISSION ENERGIES
IN
ALKALI HALIDES

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ABSTRACT

The states of an ordinary F-centre involved in absorption, emission, and step diffusion are considered on the basis of a model which represents the F-centre electron, in the adiabatic approximation, by a pseudo wave function and treats the lattice within the Born-von Kármán theory. In calculating the F-centre electron-ion interaction the ions are treated as point charges but an ion-size contribution to the energy which arises from optimizing the pseudopotential is included. Relaxation of the lattice is included by allowing all the ions in the vicinity of the defect to move, using an adaptation of the Kanzaki[8] method due to Stoneham.[10] However, electronic polarization is omitted.

The absorption, emission and step diffusion activation energies were calculated for NaCl and KCl using Born-Mayer and inverse power forms for the repulsive interaction. The absorption energies agreed well with experiment but the emission energies showed poor agreement. For KCl the step diffusion activation energy, which involves the energy difference between the relaxed F-centre excited state and the antisymmetric saddle-point state (figure 1), agreed moderately well with the experimental value after a correction was made to the zeroth order energy calculation. This correction was applied because the parameters in the repulsive interaction, evaluated from bulk equilibrium data, differ from those which must be used when the equilibrium ionic spacing differs

appreciably from the normal bulk values, as occurs for several ions near the saddle-point.

CONTENTS

CHAPTER I

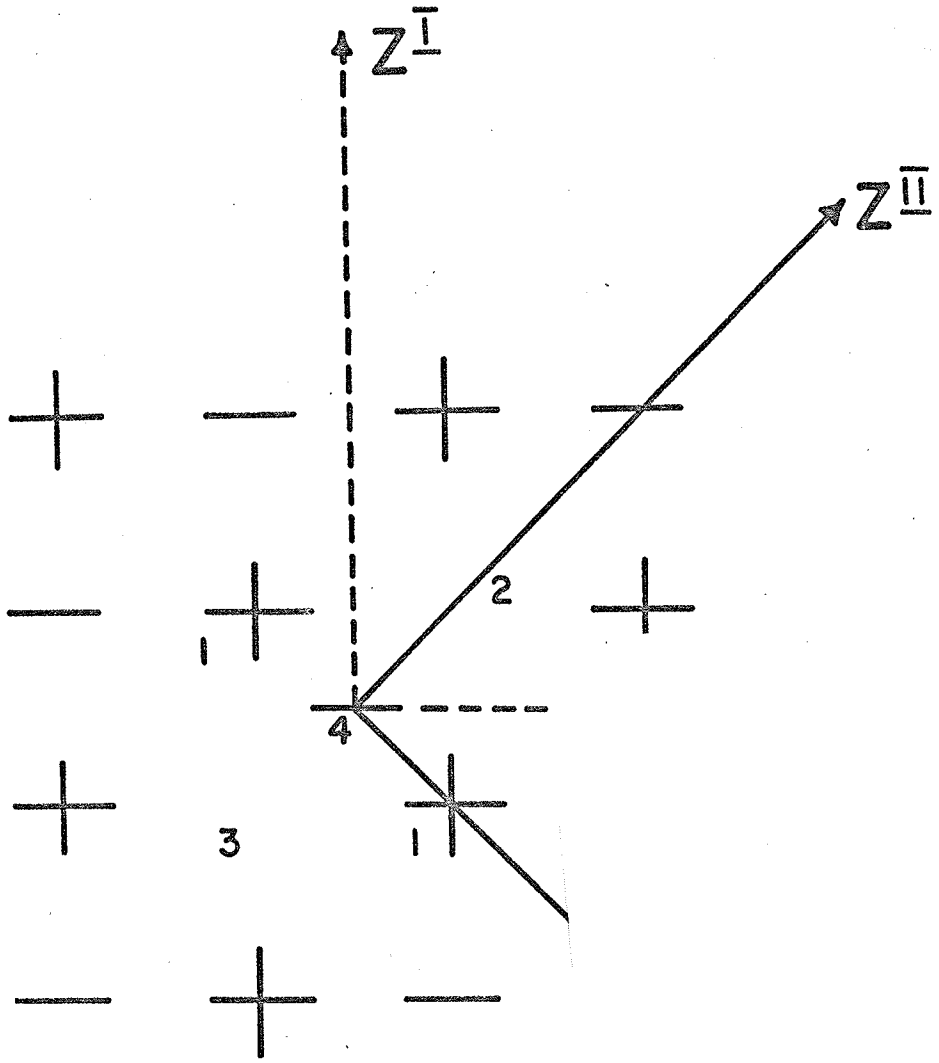
INTRODUCTION

The aim of this work was the calculation of the activation energy for one of the processes responsible for the diffusion of F-centres in alkali halide crystals, namely the F-centre step diffusion process.[1] This is the process by which a (110), second nearest neighbour, ion to an F-centre interchanges positions with the F-centre. In the other process contributing to F-centre diffusion an F-centre electron is thermally ionized to the conduction band, drifts through the crystal, and is trapped at a distant anion vacancy. The calculation of the activation energy for F-centre step diffusion involves the determination of the difference in energy of the system, including excess electron plus lattice, in the relaxed ground and excited states of the F-centre and the energy of the relaxed system in the saddle-point configuration (figure 1). In the saddle point, the electron can be in a symmetric or an antisymmetric state; consequently it is necessary to calculate the relaxed energy of both of these states. My treatment of these problems shall be described briefly below and in more detail in the appropriate sections to follow.

One of the significant results of this work has been the development of computer programs which are easily adaptable to the treatment of F_A, F_B, and F_C centres which are of considerable experimental and theoretical interest.[2,3]

FIGURE 1.

Saddle-point configuration. The ions labelled 1 are referred to in the text as group 1 ions.


Z^I
Z^II
2
1
4
3
1

These centres are modified F-centres in that the F_A, F_B and F_C centres contain respectively one, two, and three impurity alkali ions adjacent to the F-centre.

Associated with the F_A-centre there are two excitation energies. These are a reorientation energy and a dissociation energy which are the energies required to go from the initial configuration given by figure 2(a) to the configurations in figures 2(b) and 2(c) respectively. The reorientation energy may be determined in exactly the same way as the activation energy for F-centre step diffusion was determined, only one must take account of the fact that an impurity ion is present (this will modify the ion-ion interaction, the electron-ion interaction and perhaps the symmetry of the wave function of the electron). In the same manner the dissociation energy of F_A-centres and the excitation energies of F_B and F_C centres may be calculated from the same basic computer programs with the appropriate modifications.

The main problems which are involved in energy calculations are in the specification of:

(i) the wave function to describe the excess electron

(ii) the potential describing the interaction between the excess electron and the ion.

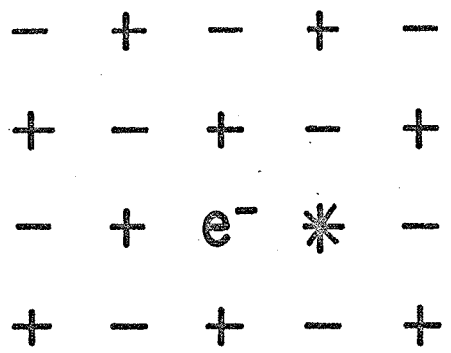
(iii) the displacements and polarizations of the ions surrounding the vacancy.

My treatment of these will be described in the following sections.

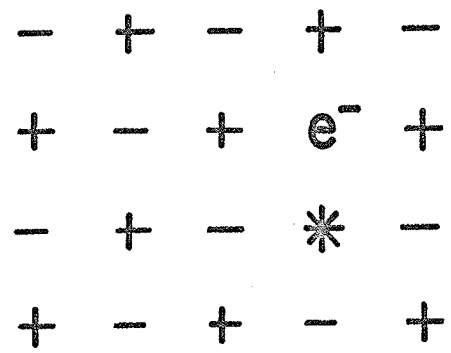
Since it was necessary to calculate the relaxed energy of the system when the F-centre electron was in its ground

FIGURE 2.

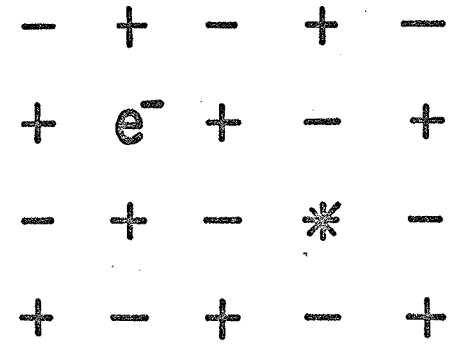
Configurations associated with the reorientation and dissociation energies of F_A-centres. * denotes an impurity cation and e^- denotes the trapped electron.



(a)



(b)



(c)

and excited states, as an added feature the absorption and emission energies for F-centres were calculated. The experimental values for these quantities are readily available,[4] hence one has some indication of the validity of the model.

The energy of the system was minimized with respect to the displacements of the ions in the crystal and the variational parameters. This was done within the framework of the pseudopotential theorem[5,6,7] which allows one to describe the excess F-centre electron by a smooth pseudo wave function and treat the change in energy of the system when it relaxes by perturbation theory. The crystal was treated within the Born-von Kármán theory, that is in the harmonic approximation, and it was assumed that the electron obeys the adiabatic approximation. This means that the electron follows the motion of the ions instantaneously or in other words the wave function of the excess electron is that which it would be if the ions were static, occupying their instantaneous positions. One also assumes in this theory that the actual crystal can be replaced by an infinite crystal with a periodicity of macroscopic dimensions. This introduction of cyclic boundary conditions replaces the actual crystal having a free surface by a hypothetical crystal where the distortions are due to a regular array of defects — one defect per unit cell. This however does not affect our calculation for the distortion of the crystal.[8]

The interaction between ions was taken to be a coulomb

interaction between point ions plus a nearest neighbour short range repulsive interaction. However, the interaction between the excess electron and the ions was assumed to involve coulomb interaction with point ions plus a term which arises from optimizing the pseudopotential and is described as the ion size correction.[9]

The displacements and polarizations of the ions can be calculated by an extension to the Kanzaki method[8] due to Stoneham.[10] In the present work the ions are allowed to relax to new positions from the perfect bulk lattice configuration but the electronic polarization associated with the defect in the crystal was not considered. Some work was started on the inclusion of this polarization by means of a shell model specification of the ions in the crystal, but this was not carried through to a conclusion.

In order to determine the absorption and emission energies it was necessary to know the distortion associated with the ground and excited state relaxed F-centre, for in the calculation of, say, the absorption energy, one invokes the Franck-Condon principle which states that the lattice relaxation time is long compared to the time associated with the photon absorption process and consequently one calculates the energy of the system in the excited state in the presence of the ground state distortion. Similarly for the final state in emission, one calculates the energy of the system in the ground state in the presence of the excited state

distortion. Hence it is crucial in the calculation of these energies that the distortions associated with the relaxed ground and excited state F-centres be determined accurately.

These calculations were carried out for KCl and NaCl for two different forms of the repulsive potential, namely a Born-Mayer repulsive potential ($Ae^{-r/\rho}$) and an inverse power form (A/r^m). This latter potential form was introduced because it was suspected that the Born-Mayer form might break down when one attempted to push ions too closely together as might occur for the saddle point configuration.

The results obtained for the F-centre absorption energies agree quite well with experiment[4] while the results for emission for both crystals considered are found to be smaller than the experimental values, thus implying a larger Stokes shift. The activation energy for F-centre step diffusion does not agree with the value quoted by Wolf[1] until one makes a correction to the zeroth order energy. This is motivated by the fact that the repulsive interaction parameters used were those for ions separated by their crystal equilibrium spacing, while at the saddle point the separation between ions is considerably less than this.

Furthermore, it was found that the splitting between the energy levels of the symmetric and antisymmetric states of the saddle-point is of the same order of magnitude as the splittings given by Gramm[11] for splitting between the symmetric and antisymmetric states of the F_A-centre. The

F_A centre (in the saddle-point configuration) differs from my saddle-point configuration only by the substitution of a neighbour impurity ion and consequently order of magnitude agreement in the splitting of these two cases is expected.

The remainder of the thesis will be divided into three chapters labelled II, III, and IV. Chapter II is intended to provide a background to the pseudopotential theory, the Kanzaki-Stoneham method of treating lattice distortion, and the shell model treatment of the ions in a crystal. The presentation of these theories in the literature is at times quite vague and usually spread over several papers. It is hoped that this section, although containing no new theory, will afford the reader an easier understanding of the methods.

Chapter III will deal with the calculations and discussion of the results of the application of this theory to the F-centre and saddle point defect while Chapter IV will give a brief summary of the results.

CHAPTER II

THEORETICAL BACKGROUND

2.1 PSEUDOPOTENTIAL METHOD

A. INTRODUCTION

It has been found that very crude models have been able to predict the observed properties of electrons to a degree which one would not have expected from the outset. For instance, good success has been obtained for calculations based on hydrogenic models for atomic energy level calculations, point ion models for crystal calculations, and nearly free electron models for the calculation of the energy of valence electrons in metals. A common feature of all these models is that the core electrons of the atoms are either ignored or treated in a very simplified manner. For example, to calculate the energy bands for the valence electrons in a crystal using the nearly free electron model one assumes that the potential energy seen by the electron is weak. Physically this is not true.

However, this model is successful due to the cancellation between the negative potential energy of the electron near an atomic nucleus and the positive kinetic energy associated with the rapid fluctuations of the wave function in this vicinity. Mathematically these rapid oscillations are a consequence of the requirement that the wavefunction of the valence electron be orthogonal to the occupied core orbitals (i.e. they are eigenfunctions of the same hermitian

Hamiltonian belonging to different eigenvalues.)

This cancellation of the potential and kinetic energy forms the justification for the use of a pseudopotential and a pseudo wave function in the calculation of electronic energy levels.[6] Although this method was originally applied to band structure calculations it is also applicable to the present problem, namely that of electrons trapped by the potential wells of crystal defects.

B. THE GENERAL PSEUDOPOTENTIAL THEOREM

The pseudopotential theorem is based on three fundamental approximations. These are:

(1) the self-consistent field approximation. This amounts to replacing the interaction between electrons by a potential that depends on some average interaction. However, this potential depends upon the states occupied by the electrons and these states depend on the potential; consequently a self-consistent calculation is necessary. Between electrons the only important interaction is the coulomb interaction which is divided into three parts.

(a) the Hartree potential which is arrived at by computing the time average of the electron distribution and then by using Poisson's equation one can obtain the corresponding potential.

(b) the correction due to the Pauli exclusion principle which gives rise to an exchange interaction.

(c) the remaining interaction which arises from the

correlated motion of the electrons.

(2) the separation of the electronic states into core and valence states and the treatment of the core states as being localized. This small core approximation is used in three ways:

(a) the cores are assumed not to overlap so there is no direct interaction between ions except for their coulomb interaction.

(b) the variation over the core of the potential due to the conduction (or excess) electrons and adjacent ions is neglected. As a consequence of this the core wave functions are the same as in the isolated ion, although their energies differ from the energies of the core states of the isolated ions.

(c) the integration of products of a smooth function and core functions is simplified since the variation of the former over the ion is neglected and consequently is taken out of the integral and given the value it assumes at the ionic site.

(3) the applicability of perturbation theory in computing the energy levels of the states.

The orginal problem in this work is the calculation of the eigenvalues and eigenfunctions of

$$H|\Psi_m\rangle = E_m|\Psi_m\rangle \qquad (1)$$

where H = the Hamiltonian = T + V

T = the kinetic energy operator

V = a one electron potential which is not necessarily local

n = c denotes a core orbital

and n = ν denotes a state of the trapped electron.

To solve equation (1) one considers the following related eigenvalue problem (equation (2)) and postulates that this equation has the same energy eigenvalues for the states of the trapped electron (i.e. for n = ν).

$$(H+V_R)|\Phi_m\rangle = \tilde{E}_m|\Phi_m\rangle \qquad (2)$$

where

$$V_R|\Phi_m\rangle = \sum_c \langle F_c|\Phi_m\rangle|\Psi_c\rangle \qquad (3)$$

and the F_c are completely arbitrary functions. This arbitrariness in the pseudopotential can be removed by placing various conditions on the potential. In our case the condition that $|\Phi\rangle$ be as smooth as possible is invoked. This corresponds to minimizing the kinetic energy of $|\Phi\rangle$, or since the energy of the system in a given state is a fixed value, to maximizing the expectation of the pseudopotential using the pseudo wave function.

The motivation for considering an eigenvalue equation of this form stems from the work related to the energy levels of conduction electrons in metals where the wave function of the conduction electron is expanded as a linear combination of plane waves which are orthogonalized to the core orbitals.[7]

Consider now the form of the pseudo wave functions which this dictates. First consider the pseudo core states and expand them as a linear combination of $\{\Psi_m\}$, which

form a complete orthonormal set.

$$|\Phi_c\rangle = \sum_{v'} \alpha^c_{v'} |\Psi_{v'}\rangle + \sum_{c'} \alpha^c_{c'} |\Psi_{c'}\rangle \qquad (4)$$

Substituting this into equation (2) one obtains

$$\sum_{c'} \sum_{c''} \left\{ (E_{c''} - \tilde{E}_c)\, \delta_{c'c''} + \langle F_{c''} | \Psi_{c'} \rangle \right\} \alpha^c_{c'} |\Psi_{c''}\rangle$$

$$+ \sum_{c''} \sum_{v'} \alpha^c_{v'} \langle F_{c''} | \Psi_{v'} \rangle |\Psi_{c''}\rangle + \sum_{v'} (E_{v'} - \tilde{E}_c) \alpha^c_{v'} |\Psi_{v'}\rangle = 0 \qquad (5)$$

Since the $|\Psi_m\rangle$ are all linearly independent, the $\alpha^c_{v'} = 0$ provided there is no accidental degeneracy (i.e. $E_{v'} = \tilde{E}_c$). Hence one is left with a set of equations to determine the $\alpha^c_{c'}$. It follows from $\alpha^c_{v'} = 0$ that the core pseudo states $|\Phi_c\rangle$ are a linear combination of only the actual core states.

$$|\Phi_c\rangle = \sum_{c'} \alpha^c_{c'} |\Psi_{c'}\rangle \qquad (6)$$

and that these core pseudo states are of no interest in calculating the actual core states of the crystal (this will be shown later).

In a similar manner consider expanding the states $|\Phi_v\rangle$ as a linear combination of the $|\Psi_m\rangle$.

Thus $$|\Phi_v\rangle = \sum_{v'} \alpha^v_{v'} |\Psi_{v'}\rangle + \sum_{c'} \alpha^v_{c'} |\Psi_{c'}\rangle$$

and again substituting into equation (2) one obtains

$$\sum_{c''} \sum_{c'} \left\{ (E_{c''} - \tilde{E}_v)\, \delta_{c'c''} + \langle F_{c''} | \Psi_{c''} \rangle \right\} \alpha^v_{c'} |\Psi_{c''}\rangle + \sum_{c''} \langle F_{c''} | \Psi_v \rangle \alpha^v_{v'} |\Psi_{c''}\rangle$$

$$+ \sum_{v' \neq v} \sum_{c''} \langle F_{c''} | \Psi_{v'} \rangle \alpha^v_{v'} |\Psi_{c''}\rangle + (E_v - \tilde{E}_v) \alpha^v_v |\Psi_v\rangle$$

$$+ \sum_{v' \neq v} (E_{v'} - \tilde{E}_v) \alpha^v_{v'} |\Psi_{v'}\rangle = 0$$

Again unless there is an accidental degeneracy $\alpha^v_{v'} = 0$ for $v' \neq v$ and hence $|\Phi_v\rangle = |\Psi_v\rangle + \sum_{c'} \alpha^v_{c'} |\Psi_{c'}\rangle \qquad (7)$

where $$\alpha^{v}_{c'} = \langle \Phi_v | \Psi_{c'} \rangle$$

and the α^{v}_{m}'s have been redefined so as to make $\alpha^{v}_{v} = 1$.

This may be rewritten as $$|\Psi_v\rangle = (1-P)|\Phi_v\rangle \qquad (8)$$

where $P = \sum_{c'} |\Psi_{c'}\rangle\langle\Psi_{c}|$ is a projection operator which projects on to the sub-space spanned by the core states. It is to be noted that the pseudo wave function so defined is not unique. One may add to equation (7) a linear combination of core states without changing the result. That is

$$|\Phi_v\rangle \longrightarrow |\Phi_v\rangle + \sum_{c'} b_{c'} |\Psi_{c'}\rangle \qquad (9)$$

and when this is substituted into equation (8) one sees that the actual wave function of the system is not changed. It should be emphasized that having found $|\Phi_v\rangle$ one need only orthogonalize this to the actual core states to obtain the actual excess electron wave function.

It has been stated that this is true if there is no accidental degeneracy. If an accidental degeneracy does arise this just introduces a further arbitrariness into the wave function, but it may still be chosen in the form given by equations (6) and (7).

The pseudopotential which was defined by equation (3) contains the arbitrary functions F_c. These can now be fixed by optimizing the pseudopotential. The criterion which is used is that $|\Phi\rangle$ be the smoothest possible $|\Phi\rangle$, that is the oscillations in the actual wave function at the ion core sites, which result mathematically from the requirement that $|\Psi_v\rangle$

be orthogonal to the core orbitals, be subtracted out as well as possible. Alternately, since the energy of the system in a given state is constant, one may apply the variation method to maximize

$$\frac{\langle \Phi | V+V_R | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

To consider the variation of this expression one introduces a Lagrangian multiplier λ and considers

$$\delta \left(\langle \Phi | V+V_R | \Phi \rangle - \lambda \langle \Phi | \Phi \rangle \right) = 0$$

$$\langle \delta\Phi | V+V_R | \Phi \rangle + \langle \Phi | V+V_R | \delta\Phi \rangle - \lambda \langle \delta\Phi | \Phi \rangle - \langle \Phi | \delta\Phi \rangle = 0$$

Since in the general case $|\Phi\rangle$ is complex one may consider the variation of $|\Phi^+\rangle$ and $|\Phi\rangle$ separately, hence this equation becomes

$$\langle \delta\Phi | V+V_R | \Phi \rangle - \lambda \langle \delta\Phi | \Phi \rangle = 0 \qquad (10)$$

Since this is true for arbitrary variations of $|\Phi\rangle$

$$(V+V_R)|\Phi\rangle - \lambda |\Phi\rangle = 0$$

$$\therefore \quad \lambda = \frac{\langle \Phi | V+V_R | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \bar{V}$$

Thus equation (10) becomes

$$\langle \delta\Phi | V+V_R | \Phi \rangle - \bar{V} \langle \delta\Phi | \Phi \rangle = 0 \qquad (11)$$

Since $\delta\Phi$ is arbitrary we shall choose $|\delta\Phi\rangle = \sum_c' b_c |\Psi_c\rangle$ (we have seen that the addition of this $\delta\Phi$ to Φ does not change the actual wave function of the system.) Hence substituting into equation (11) one obtains

$$\sum_c' b_c \left[\langle \Psi_c | V+V_R | \Phi \rangle - \bar{V} \langle \Psi_c | \Phi \rangle \right] = 0$$

Since this is true for arbitrary b_c then

$$\langle \Psi_c | V+V_R | \Phi \rangle - \bar{V} \langle \Psi_c | \Phi \rangle = 0 \qquad (12)$$

From equation (3)

$$(V+V_R)|\Phi\rangle = V|\Phi\rangle + \sum_{c'}' |\Psi_{c'}\rangle \langle F_{c'} | \Phi \rangle$$

Thus taking the inner product on the left with $\langle \Psi_c |$

$$\langle \Psi_c | V+V_R | \Phi \rangle = \langle \Psi_c | V | \Phi \rangle + \langle F_c | \Phi \rangle$$

and substituting for $\langle \Psi_c | V+V_R | \Phi \rangle$ in equation (12) one obtains $\langle \Psi_c | V | \Phi \rangle + \langle F_c | \Phi \rangle = \bar{V} \langle \Psi_c | \Phi \rangle$

$$\therefore \langle F_c | \Phi \rangle = \langle \Psi_c | \bar{V} - V | \Phi \rangle \qquad (13)$$

Finally substituting for $\langle F_c | \Phi \rangle$ into equation (3) one obtains the optimum pseudopotential.

$$V_R | \Phi \rangle = \sum_c' | \Psi_c \rangle \langle \Psi_c | \bar{V} - V | \Phi \rangle$$

or $$V_R | \Phi \rangle = P(\bar{V} - V) | \Phi \rangle \qquad (14)$$

It is necessary to comment further on the core pseudo eigenvalues and eigenfunctions. In a practical application of the pseudopotential method one usually employs a minimization procedure to fix various parameters in the problem. Hence it is essential that the lowest eigenstates of H for the trapped electron should correspond to the lowest eigenstates of $H+V_R$. To see that this is so, consider the following equation which comes from the requirement that equation (5) have a non-trivial solution.

$$\det | (E_{c''} - \tilde{E}_c) \delta_{c'c''} + \langle F_{c''} | \Psi_{c'} \rangle | = 0$$

$$\therefore \det | (E_{c''} - \tilde{E}_c) \delta_{c'c''} + \langle \Psi_{c''} | \bar{V} - V | \Psi_{c'} \rangle | = 0$$

The off-diagonal elements of this matrix are small since this involves the matrix element of V between core orbitals centred on different ions. Hence one diagonal element must be zero $(E_{c'} - \tilde{E}_c) + \bar{V} - \langle \Psi_{c'} | V | \Psi_{c'} \rangle \approx 0$

$$\therefore \tilde{E}_c \approx \bar{V} + T_{c'}$$

where $T_{c'}$ is the kinetic energy of the electron in the state $|\Psi_{c'}\rangle$ and since for localized core states $T_{c'} > T_v$ hence

$$\tilde{E}_{c'} > \bar{V} + T_v = \tilde{E}_v \quad \text{where } T_v = \langle \Phi_v | T | \Phi_v \rangle \text{ and}$$

since $|\Phi_v\rangle$ is the smoothest $|\Phi_v\rangle$ possible. Hence the core pseudo states lie above the lowest eigenstates of $(H+V_R)$.

Thus to solve the eigenvalue problem $H|\Psi_m\rangle = E_m|\Psi_m\rangle$ one considers a related eigenvalue problem

$$(H+V_R)|\Phi_m\rangle = \tilde{E}_m|\Phi_m\rangle$$

where

$$|\Psi_m\rangle = (1-P)|\Phi_m\rangle$$

$$V_R|\Phi_m\rangle = P(\bar{V}-V)|\Phi_m\rangle$$

and $|\Phi_m\rangle$ is the smoothest possible wave function.

C. ION SIZE EFFECT

In this section we summarize the treatment of Bartram, Stoneham, and Gash (BSG)[9] of the finite size of the ions of the crystal. This finite size is taken into account in the interaction between the trapped electron and the ions within the framework of the pseudopotential theory. From equation (14) one can separate out the point ion contribution as

$$V_P = V + V_R = V_{PI} + (V - V_{PI}) + P(\bar{V} - V) \qquad (15)$$

where V_{PI} = the point ion potential, that is the potential energy operator when the crystal ions are treated as point charges. The latter two terms in equation (15) may be considered as the ion size correction in the pseudopotential just as $(V-V_{PI})$ is in the actual potential. As a consequence of the assumption that the ion core orbitals on different ions do not overlap one may write

$$P = \sum_{\gamma}' P_\gamma$$

$$V = \sum_{\gamma}' V_\gamma$$

and $$V_{PI} = \sum_{\gamma}' V_{PI\gamma}$$

where γ refers to a particular ion.

Hence $$V_P = V_{PI} + \sum_{\gamma}' \left[(1-P_\gamma)(V_\gamma - V_{PI\gamma}) - P_\gamma V_{PI\gamma} + P_\gamma(\bar{V} - U_\gamma) \right]$$

where $$U_\gamma = \sum_{\gamma' \neq \gamma}' V_{\gamma'} \approx \sum_{\gamma' \neq \gamma}' V_{PI\gamma'}$$

where this last approximation arises from the assumption that the ion core orbitals are highly localized on a particular centre. Hence from outside the ion V_γ and $V_{PI\gamma}$ appear approximately the same. The assumption that the pseudo wave function is smooth is used to simplify the large number of two centre integrals which are present. That is the variation of Φ over the core orbitals is neglected and hence it is taken out of the integral and replaced by its value at the ion centre. Consequently one may write

$$\langle \Phi | V_P | \Phi \rangle = \langle \Phi | V_{PI} | \Phi \rangle + \sum_{\gamma}' C_\gamma |\Phi(\vec{r}_\gamma)|^2 \qquad (16)$$

where $$C_\gamma = A_\gamma + B_\gamma(\bar{V} - U_\gamma) \qquad (17)$$

$$B_\gamma = \sum_{c'}' \iint \Psi_{\gamma c'}(\vec{r}) \, \Psi^{+}_{\gamma c'}(\vec{r}') \, d\tau \, d\tau' \qquad (18)$$

and $$A_\gamma = \int \left[V_\gamma(\vec{r}) - V_{PI\gamma}(\vec{r}) \right] d\tau - \sum_{c}' \iint \Psi_{\gamma c'}(\vec{r}) V_{PI\gamma}(\vec{r}') \Psi^{+}_{\gamma c'}(\vec{r}') \, d\tau \, d\tau'$$

$$- \sum_{c'}' \iint \Psi_{\gamma c'}(\vec{r}) \left[V_\gamma(\vec{r}') - V_{PI\gamma}(\vec{r}') \right] \Psi^{+}_{\gamma c'}(\vec{r}') \, d\tau \, d\tau' \qquad (19)$$

It is to be noted that only the s-orbitals in P_γ make a non-vanishing contribution to C_γ and moreover P_γ projects out only the spherically symmetric part of U_γ which is treated as a constant in equation (16). To see this consider as an

example $\sum_{c'} \iint \Psi_{\gamma c}(\vec{r}) \Psi^{+}_{\gamma c'}(\vec{r}') V_{PI\gamma}(\vec{r}') d\tau d\tau'$

First consider expanding $V_{PI\gamma}(\vec{r}')$ as a linear combination of spherical harmonics. Now integrate over the primed variables; this gives a zero result unless the ℓ values for $\Psi^{+}_{\gamma c}(\vec{r}')$ and $V_{PI\gamma}(\vec{r}')$ are the same and then the result of the integration is a constant. Hence when the integration over the unprimed variables is performed a non-zero contribution occurs only for the $\ell = 0$. Hence P_γ projects out only the spherically symmetric part of U_γ (note that this is a consequence of the fact that the variation of Φ over the ion cores is neglected). It should also be noted that U_γ depends on the crystal structure.

The coefficients A_γ and B_γ have been calculated by BSG[9] for a large number of ions with closed shell configurations. The A_γ and B_γ are characteristic only of the ions and not of the crystal as free ion orbitals were used in the calculation. Note in their calculation for the electron-electron interaction that correlation is neglected; that is they consider only the Hartree potential and exchange.

It was found by BSG[9] that in order to get good agreement with experiment for the F-band absorption energy it was necessary to reduce A_γ by .53. The same value of the correction factor for A_γ was found to be applicable to F-centre absorption energies in the alkali halides and alkaline-earth fluorides. Consequently BSG propose that a set of

semi-empirical pseudopotential coefficients be used in colour centre calculations which incorporate this factor. It is not apparent what shortcoming of the theoretical treatment necessitates the introduction of this factor.

Finally it should be noted that the calculation of the ion size effect involves the self-consistent determination of $\bar{V} = \langle \Phi | V_p | \Phi \rangle$ which is contained in equation (16).

2.2 KANZAKI-STONEHAM METHOD FOR CALCULATING LATTICE RELAXATION

A. GENERAL FORMULATION

A great deal of the work on lattice distortions around defects has been patterned after the approach of Mott and Littleton[12] which combines an atomistic calculation of the relaxation of the nearest neighbours with a dielectric description of the long range polarization effects. In the present work one expects that these polarization effects will be small since from a distance the defects appear neutral. Hence an approach based on an adaptation of the Kanzaki[8,13] method due to Stoneham[10] was used which considers the distortion associated with each ion separately. In such a treatment of the distortion one considers a perfect lattice which has the same distortion field as the defect lattice (only the defect is not present). The energy of the lattice is then corrected to account for the fact that there actually is a defect. This calculation is performed within the framework of the harmonic approximation; that is it is assumed that in a Taylor expansion of the energy of the system it is necessary to include terms up to and including only second order in the displacements and polarizations of the crystal ions.

To illustrate this method consider an excess electron defect where the electron is described by a pseudo wave function Φ, containing variation parameters $\underline{\lambda}$. (In general $\underline{\lambda}$ contains all the defect parameters, and may include, for example, the zeroth order displacement of an ion, if it exceeds the

limits of the harmonic approximation). First consider a lattice with no defect present but with the distortion field which would result if the defect were introduced. The energy of this system may be written as

$$E(\underline{\underline{\xi}}) = U_o + \frac{1}{2}\,\underline{\xi}\cdot\underline{\underline{A}}\cdot\underline{\xi}$$

where U_o = the energy of the perfect lattice when the distortion field is zero.

$\underline{\xi}$ = a column matrix representing the resultant distortion field of the crystal

and $\underline{\underline{A}}$ = the force constant matrix for a perfect crystal.

Now consider introducing a defect into the crystal. The energy of the system now becomes

$$E(\underline{\xi},\underline{\lambda}) = U_o + \frac{1}{2}\,\underline{\xi}\cdot\underline{\underline{A}}\cdot\underline{\xi} + \Delta E(\underline{\xi},\underline{\lambda}) \qquad (20)$$

where $\underline{\lambda}$ = a column matrix representing the variational parameters and $\Delta E(\underline{\xi},\underline{\lambda})$ = the change in energy of the distorted lattice due to the introduction of the defect.

$\Delta E(\underline{\xi},\underline{\lambda})$ may be written as

$$\Delta E(\underline{\xi},\underline{\lambda}) = T(\underline{\lambda}) + V(\underline{\xi},\underline{\lambda}) + V_L(\underline{\xi}) \qquad (21)$$

where $T(\underline{\lambda})$ = the kinetic energy of the electron

$V(\underline{\xi},\underline{\lambda})$ = the electron-lattice interaction energy in the presence of lattice distortion

and $V_L(\underline{\xi})$ = the change in lattice energy caused by the introduction of the defect.

Hence expanding this energy to quadratic terms in $\underline{\xi}$, and $\underline{\lambda}$ one obtains

$$\Delta E(\underline{\xi},\underline{\lambda}) = U_o + \Delta E(\underline{o},\underline{\lambda}_o) + \frac{1}{2}\,\underline{\xi}\cdot\underline{\underline{A}}\cdot\underline{\xi} + \underline{F}_o\cdot\underline{\xi} + \frac{1}{2}\,\underline{\xi}\cdot\underline{\underline{F}}'\cdot\underline{\xi}$$

$$+(\underline{\lambda}-\underline{\lambda}_o)\cdot\underline{\underline{\Lambda}}\cdot\underline{\xi} + \frac{1}{2}\,(\underline{\lambda}-\underline{\lambda}_o)\cdot\underline{\underline{\Lambda}}'\cdot(\underline{\lambda}-\underline{\lambda}_o) \qquad (22)$$

where $\underline{\lambda}_o$ are the values of the variation parameters obtained by ignoring distortion of the crystal and $\underline{F}_o$, $\underline{\underline{F}}'$, $\underline{\underline{\Lambda}}$, and $\underline{\underline{\Lambda}}'$ are defined as follows

$$\underline{F}_o = \left[\frac{\partial \Delta E(\underline{\xi},\underline{\lambda})}{\partial \underline{\xi}}\right]_o$$

$$\underline{\underline{F}}' = \left[\frac{\partial^2 \Delta E(\underline{\xi},\underline{\lambda})}{\partial \underline{\xi}\ \partial \underline{\xi}}\right]_o$$

$$\underline{\underline{\Lambda}} = \left[\frac{\partial^2 \Delta E(\underline{\xi},\underline{\lambda})}{\partial \underline{\xi}\ \partial(\underline{\lambda}-\underline{\lambda}_o)}\right]_o$$

and

$$\underline{\underline{\Lambda}}' = \left[\frac{\partial^2 \Delta E(\underline{\xi},\underline{\lambda})}{\partial^2(\underline{\lambda}-\underline{\lambda}_o)}\right]_o$$

where the o after the derivatives means that they are evaluated with $\underline{\xi}=\underline{0}$ and $\underline{\lambda}=\underline{\lambda}_o$.

The procedure now is to minimize the energy of the system with respect to the parameters $\underline{\lambda}$ and distortions $\underline{\xi}$. (It should be noted that in general $\underline{\xi}$ will correspond to the three components of displacement and three components of the dipole moment of all the ions).

Thus considering $\frac{\delta}{\delta(\underline{\lambda}-\underline{\lambda}_o)} E(\underline{\xi},\underline{\lambda}) = 0$

one obtains

$$\underline{\lambda}-\underline{\lambda}_o = -(\underline{\underline{\Lambda}}')^{-1}\cdot\underline{\underline{\Lambda}}\cdot\underline{\xi} \qquad (23)$$

since all the matrices involved are symmetrical.

Substituting this result of equation (23) back into equation (22) one obtains

$$E(\underline{\xi},\underline{\lambda}) = E(\underline{0},\underline{\lambda}_o) + \tfrac{1}{2}\,\underline{\xi}\cdot\underline{\underline{A}}\cdot\underline{\xi} + \underline{F}_o\cdot\underline{\xi} + \tfrac{1}{2}\,\underline{\xi}\cdot\underline{\underline{F}}'\cdot\underline{\xi} - \tfrac{1}{2}\,\underline{\xi}\cdot\underline{\underline{\Lambda}}\cdot(\underline{\underline{\Lambda}}')^{-1}\cdot\underline{\underline{\Lambda}}\cdot\underline{\xi} \qquad (24)$$

where

$$E(\underline{0},\underline{\lambda}_o) = U_o + \Delta E(\underline{0},\underline{\lambda}_o)$$

This is now minimized with respect to the distortions of the crystal. That is applying $\frac{S}{S\underline{\xi}} E(\underline{\xi},\underline{\lambda}) = 0$ equation (24) becomes

$$\underline{\xi}\cdot\underline{\underline{A}} + \underline{F}_0 + \underline{\xi}\cdot\underline{\underline{F}}' - \underline{\xi}\cdot\underline{\underline{\Lambda}}\cdot(\underline{\underline{\Lambda}}')^{-1}\cdot\underline{\underline{\Lambda}} = 0 \qquad (25)$$

since $\underline{\underline{A}}$, $\underline{\underline{F}}'$, $\underline{\underline{\Lambda}}$ and $\underline{\underline{\Lambda}}'$ are symmetrical matrices (that is the matrix equals its transpose).

Now upon operating on the right hand side of equation (25) with $\cdot\underline{\xi}$ one can obtain an expression for $\underline{\xi}\cdot\underline{\underline{A}}\cdot\underline{\xi}$ which is then substituted back into equation (24) to obtain an expression for the relaxed energy of the system.

$$E(\underline{\xi},\underline{\lambda}) = E(\underline{0},\underline{\lambda}_0) + \tfrac{1}{2}\,\underline{F}_0\cdot\underline{\xi} \qquad (26)$$

In this expression for the relaxed energy of the system it appears that there is no contribution from the change in the variational parameters $\underline{\lambda}$ to the relaxation. This is not true since one calculates the distortion field from equation (25) which does involve $\underline{\underline{\Lambda}}$ and $\underline{\underline{\Lambda}}'$ which are matrices whose elements are derivatives of $\Delta E(\underline{\xi},\underline{\lambda})$ with respect to $(\underline{\lambda}-\underline{\lambda}_0)$.

To calculate the distortion field consider rewriting equation (25) as

$$\underline{\xi}\cdot\underline{\underline{A}} = -\underline{F}_0 + \underline{\xi}\cdot\underline{\underline{\beta}} \qquad (27)$$

where $$\underline{\underline{\beta}} = -\underline{\underline{F}}' + \underline{\underline{\Lambda}}\cdot(\underline{\underline{\Lambda}}')^{-1}\cdot\underline{\underline{\Lambda}} \qquad (28)$$

or from the transpose of equation (27)

$$\underline{\xi} = \underline{\underline{A}}^{-1}\cdot\left[-\underline{F}_0 + \underline{\underline{\beta}}\cdot\underline{\xi}\right] = -\underline{\underline{A}}^{-1}\cdot\underline{F} \qquad (29)$$

where $$\underline{F} = \underline{F}_0 - \underline{\underline{\beta}}\cdot\underline{\xi} \qquad (30)$$

The actual solution of equation (29) is based on the fourier transform of $\underline{\xi} = -\underline{\underline{A}}^{-1}\cdot\underline{F}$

which directly involves the dynamical matrix of the perfect lattice through $\underline{\underline{A}}$. Further details will appear in Chapter III.

It should be mentioned that electronic polarization of the ions may be included in the calculation by the introduction of a shell model representation for the ions. This shell model will be described in the next section.

To see how one introduces the fourier transform and the dynamical matrix consider rewriting equation (29) as

$$-F_\alpha(\vec{r}_K^{\,\ell}) = \left[\underline{\underline{A}}\cdot\underline{\xi}\right]_\alpha = \sum_{\ell',K',\beta}\left[\frac{\partial^2 U}{\partial \xi_\alpha(\vec{r}_K^{\,\ell})\,\partial \xi_\beta(\vec{r}_{K'}^{\,\ell'})}\right]_0 \xi_\beta(\vec{r}_{K'}^{\,\ell'}) \qquad (31)$$

where $\xi_\alpha(\vec{r}_K^{\,\ell})$ = the α^{th} component of the displacement or dipole moment of the K^{th} ion in the ℓ^{th} unit cell, whose position is $\vec{r}_K^{\,\ell}$.

U = the energy of a lattice (without a defect) which has the same distortion field as the defect lattice.

and $F_\alpha(\vec{r}_K^{\,\ell})$ = the α^{th} component of $\underline{F}$ which is defined by equation (30).

The solution of equation (31) involves the solution of a large number of inhomogeneous linear equations in the ionic displacements and dipole moments. In order to simplify this problem one introduces a fourier transform by

$$\xi_\alpha(\vec{r}_K^{\,\ell}) = \sum_{\vec{q}} Q_\alpha^K(\vec{q})\, e^{-i\vec{q}\cdot\vec{r}_K^{\,\ell}} \qquad (33)$$

where $\vec{q}$ is restricted in range by the periodic boundary conditions. That is the number of allowed values of $\vec{q}$ is equal to the number of unit cells in the crystal. Thus substituting this into equation (31) one obtains

$$\sum_{\vec{q}} G_\alpha^K(\vec{q}) e^{-i\vec{q}\cdot\vec{n}_K^\ell} + \sum_{\vec{q}}' \sum_{\ell',K',\beta} \left[\frac{\partial^2 U}{\partial \xi_\alpha(\vec{n}_K^\ell)\partial \xi_\beta(\vec{n}_{K'}^{\ell'})}\right]_0 Q_\beta^{K'}(\vec{q}) e^{-i\vec{q}\cdot\vec{n}_{K'}^{\ell'}} = 0 \tag{34}$$

where $$F_\alpha(\vec{n}_K^\ell) = \sum_{\vec{q}}' G_\alpha^K(\vec{q}) e^{-i\vec{q}\cdot\vec{n}_K^\ell} \tag{35}$$

or $$G_\alpha^K(\vec{q}) = \frac{1}{N} \sum_{\ell'} F_\alpha(\vec{n}_K^{\ell'}) e^{i\vec{q}\cdot\vec{n}_K^{\ell'}} \tag{36}$$

and N = the number of unit cells in the crystal. Thus multiplying equation (34) by $e^{i\vec{q}\cdot\vec{n}_K^{\ell''}}$ and introducing the following fourier transform

$$D_{\alpha\beta}^{KK'}(\vec{q}) = \sum_{\ell'}' \left[\frac{\partial^2 U}{\partial \xi_\alpha(\vec{n}_K^\ell)\partial \xi_\beta(\vec{n}_{K'}^{\ell'})}\right]_0 e^{-i\vec{q}\cdot(\vec{n}_{K'}^{\ell'} - \vec{n}_K^\ell)}$$

equation (34) becomes

$$\sum_{\vec{q}}' \left\{ G_\alpha^K(\vec{q}) + \sum_{K',\beta}' D_{\alpha\beta}^{KK'}(\vec{q}) Q_\beta^{K'}(\vec{q}) \right\} = 0 \tag{37}$$

Equation (37) may now be solved for $Q_\beta^{K'}(\vec{q})$ for each value of $\vec{q}$ and then using equation (33) one may solve for the displacements of the ions. In practice an iterative procedure is used to solve for the $Q_\beta^{K'}(\vec{q})$. As a first approximation one chooses $\underline{F}$ in equation (29) to be $\underline{F}_0$. That is since $\underline{\underline{\beta}}$ is a matrix whose elements are second derivatives of $\Delta E(\underline{\xi}, \underline{\lambda})$ with respect to $\underline{\xi}$ and $(\underline{\lambda} - \underline{\lambda}_0)$ and consequently small, one considers as a first approximation only the leading term $\underline{F}_0$ in $\underline{F}$. One then calculates $Q_\beta^{K'}(\vec{q})$ from equation (37) and hence $\xi_\alpha(\vec{n}_{K'}^\ell)$ from equation (33). Then as a second approximation one chooses $\underline{F} = \underline{F}_0 - \underline{\underline{\beta}} \cdot \underline{\xi}^{(0)}$ where $\underline{\xi}^{(0)}$ corresponds to the first approximation to the distortion field. One then uses equation (37) again to recalculate $Q_\beta^{K'}(\vec{q})$ and so on until

convergence is obtained.

There are several advantages to such an approach to the lattice distortion calculation. These are as follows:

(i) In equation (36) the summation over ℓ may be restricted since $F_\alpha(\vec{n}^{\ell}_{K})$ decreases with increasing distance from the defect. Also it is possible to group ions according to whether $F_\alpha(\vec{n}^{\ell}_{K})$ is the same, again cutting down the number of ions which need be considered in the summation in equation (36).

(ii) Another advantage is that the fourier transform process need be carried through only in the zeroth order calculation obtaining what I shall call distortion coefficients. It is then necessary to multiply these by the $F_\alpha(\vec{n}^{\ell}_{K})$ to carry out the iterative procedure for the $\xi_\alpha(\vec{n}^{\ell}_{K})$.

(iii) Furthermore these distortion coefficients depend only on the lattice configuration of the defect. Hence if one changes the wavefunction to describe say an electron trapped by the defect it is not necessary to recalculate these distortion coefficients; only the $F_\alpha(\vec{n}^{\ell}_{K})$. These distortion coefficients do however depend on the crystal through the dynamical matrices $D^{KK'}_{\alpha\beta}(\vec{q})$.

(iv) One is not restricted as in most methods to a consideration of the distortions of only the nearest ions to the defect. It is possible to calculate the distortion coefficients for ions as far away from the defect as you like. This involves more computing time, but since the

calculation of all the distortion coefficients need not be carried out on the same run, several runs can triple the number of ions considered very easily.

After having calculated the distortion field one may now go back to equation (23) to calculate the change in the variational parameters when the lattice is allowed to relax.

B. ABSORPTION AND EMISSION ENERGIES

As a starting point for this project it was decided to test the method of calculation by computing the F-centre absorption and emission energies since these quantities are well known from experiment.[4] To calculate the absorption energy one must first determine the ground state energy of the relaxed system, $E_g(\underline{\xi}_g, \underline{\lambda}_g)$. This corresponds to the F-centre electron being in its ground state. Throughout this discussion the subscripts g and ex shall be used to refer respectively to the ground and excited states of the system. It should be noted that $\underline{\xi}_g$ and $\underline{\lambda}_g$ then refer to the distortion field and variation parameters respectively which minimize the F-centre ground state energy. Furthermore, throughout this discussion the terminology F-centre ground state energy shall actually mean the energy of the system when the F-centre electron is in its ground state. A similar terminology shall apply for the excited state.

Having located $E_g(\underline{\xi}_g, \underline{\lambda}_g)$ one then assumes the Franck-Condon principle which states that during a radiative transition the crystal ions do not have time to relax. Hence

the energy of the unrelaxed excited F-centre, $E'_{ex}(\underline{\xi}_g, \underline{\lambda}'_{ex})$, is calculated in the presence of the ground state distortion field. The $\underline{\lambda}'_{ex}$ are the excited F-centre state variational parameters which are determined when the distortion field is $\underline{\xi}_g$. This energy level arrangement for absorption and emission is shown in figure 3. From equation (26) the energy of the relaxed ground state may be written as

$$E_g(\underline{\xi}_g, \underline{\lambda}_g) = E_g(\underline{0}, \underline{\lambda}_{0g}) + \frac{1}{2}\underline{F}_{0g}\cdot\underline{\xi}_g \qquad (38)$$

where $\underline{F}_{0g}$ is the matrix $\underline{F}_0$ of equation (26) corresponding to the F-centre ground state.

$$E_g(\underline{0}, \underline{\lambda}_{0g}) = U_0 + \langle\Phi_g|H_p|\Phi_g\rangle_0 + V_L(\underline{0})$$

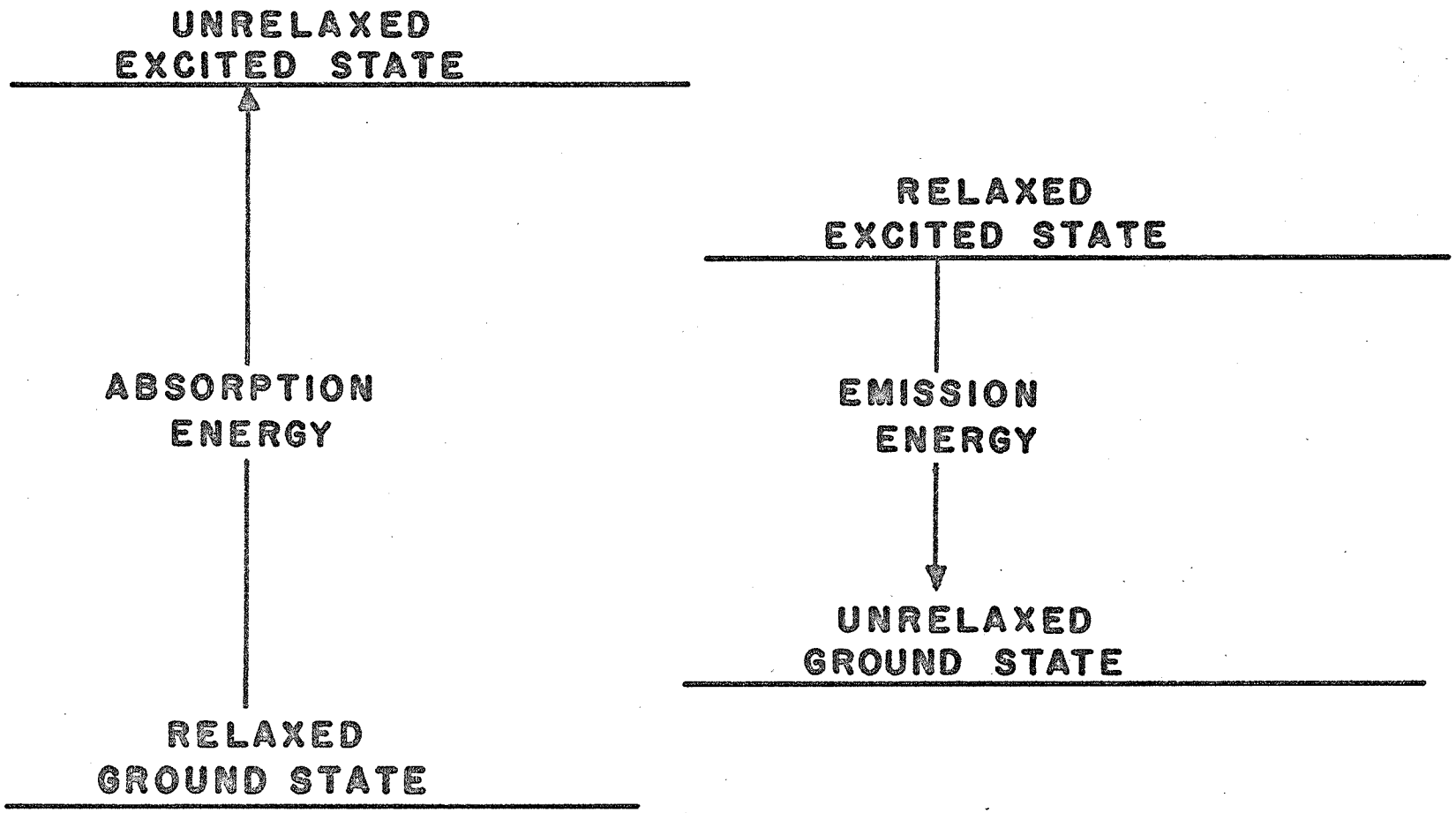
$\langle\Phi_g|H_p|\Phi_g\rangle_0$ = the expectation value of the pseudo-Hamiltonian $H_p = T + V_p$ where T is the kinetic energy operator and V_p is the pseudopotential operator, for the ground state pseudo wave function Φ_g evaluated for $\underline{\xi}_g = \underline{0}$ and $\underline{\lambda}_g = \underline{\lambda}_{0g}$ ($\underline{\lambda}_{0g}$ are the variational parameters found by minimizing $E_g(\underline{0}, \underline{\lambda}_g)$)

and $V_L(\underline{0})$ = the change in lattice energy in an undistorted lattice when a negative ion is removed.

To find the energy of the first excited state of the F-centre electron in the presence of the distortion field $\underline{\xi}_g$ one considers first a lattice containing no anion vacancy but having the distortion field $\underline{\xi}_g$. One then removes an anion from the lattice without allowing for any change in

FIGURE 3.

Absorption and emission energies of an ordinary F-centre. The energy of the unrelaxed excited state is calculated in the presence of the ground state distortion. Similarly the unrelaxed ground state energy is calculated in the presence of the excited state distortion.


UNRELAXED
EXCITED STATE
ABSORPTION
ENERGY
RELAXED
GROUND STATE
RELAXED
EXCITED STATE
EMISSION
ENERGY
UNRELAXED
GROUND STATE

the distortion field and an electron is placed into this vacancy in a state corresponding to the first excited state of an F-centre. The energy of the system may then be written as

$$E'_{ex}(\underline{\xi}_g, \underline{\lambda}'_{ex}) = U'_o + \Delta E(\underline{\xi}_g, \underline{\lambda}'_{ex}) \qquad (39)$$

where U'_o = the energy of a lattice containing no vacancy but the distortion field is $\underline{\xi}_g$.

and $\Delta E(\underline{\xi}_g, \underline{\lambda}'_{ex})$ = the change in the energy of the system that occurs when an anion is extracted and an electron is added in a state corresponding to the first excited state described by Φ'_{ex}.

But $$\Delta E'_{ex}(\underline{\xi}_g, \underline{\lambda}'_{ex}) = \langle \Phi'_{ex} | H_p | \Phi'_{ex} \rangle' + V_L(\underline{\xi}_g)$$

where the prime on the expectation value means it is evaluated with the distortion field $\underline{\xi}_g$ and variational parameters $\underline{\lambda}'_{ex}$

Also $$U'_o = U_o + \tfrac{1}{2}\, \underline{\xi}_g \cdot \underline{\underline{A}} \cdot \underline{\xi}_g$$

where $\underline{\underline{A}}$ is as before the force constant matrix for a perfect lattice. Thus the absorption energy E_a is

$$E_a(\underline{\xi}_g, \underline{\lambda}_g, \underline{\lambda}'_{ex}) = E'_{ex}(\underline{\xi}_g, \underline{\lambda}'_{ex}) - E_g(\underline{\xi}_g, \underline{\lambda}_g)$$

$$\therefore E_a(\underline{\xi}_g, \underline{\lambda}_g, \underline{\lambda}'_{ex}) = \tfrac{1}{2}\, \underline{\xi}_g \cdot \underline{\underline{A}} \cdot \underline{\xi}_g + V_L(\underline{\xi}_g) + \langle \Phi'_{ex} | H_p | \Phi'_{ex} \rangle'$$

$$- \langle \Phi_g | H_p | \Phi_g \rangle_o - V_L(\underline{o}) - \tfrac{1}{2}\, \underline{F}_{og} \cdot \underline{\xi}_g \qquad (40)$$

But from equation (27)

$$\underline{\xi}_g \cdot \underline{\underline{A}} \cdot \underline{\xi}_g = -\underline{F}_{og} \cdot \underline{\xi}_g - \underline{\xi}_g \cdot \underline{\underline{F}}'_g \cdot \underline{\xi}_g + \underline{\xi}_g \cdot \underline{\underline{\Lambda}}_g \cdot (\underline{\underline{\Lambda}}'_g)^{-1} \cdot \underline{\underline{\Lambda}}_g \cdot \underline{\xi}_g \qquad (41)$$

thus substituting into equation (40) one obtains

$$E_a(\underline{\xi}_g, \underline{\lambda}_g, \underline{\lambda}'_{ex}) = \left[\langle \Phi'_{ex} | H_p | \Phi'_{ex} \rangle' - \langle \Phi_g | H_p | \Phi_g \rangle_o\right] + \left[V_L(\underline{\xi}_g) - V_L(\underline{o})\right] - \left[\underline{F}_{og} \cdot \underline{\xi}_g + \tfrac{1}{2} \underline{\xi}_g \cdot \underline{\underline{F}}'_g \cdot \underline{\xi}_g - \tfrac{1}{2} \underline{\xi}_g \cdot \underline{\underline{\Lambda}}_g \cdot (\underline{\underline{\Lambda}}'_g)^{-1} \cdot \underline{\underline{\Lambda}}_g \cdot \underline{\xi}_g\right] \quad (42)$$

In a similar manner one can also obtain an expression for the emission energy, E_{em}, of an F-centre

$$E_{em}(\underline{\xi}_{ex}, \underline{\lambda}_{ex}, \underline{\lambda}'_g) = E_{ex}(\underline{\xi}_{ex}, \underline{\lambda}_{ex}) - E'_g(\underline{\xi}_{ex}, \underline{\lambda}'_g)$$

where $E_{ex}(\underline{\xi}_{ex}, \underline{\lambda}_{ex})$ = the energy of the relaxed F-centre excited state and $\underline{\xi}_{ex}$ and $\underline{\lambda}_{ex}$ are the corresponding values for the distortion field and variational parameters

and $E'_g(\underline{\xi}_{ex}, \underline{\lambda}'_g)$ = the energy of the unrelaxed F-centre ground state immediately following de-excitation and the $\underline{\lambda}'_g$ are the variational parameters corresponding to this state.

Similarly as before

$$E_{ex}(\underline{\xi}_{ex}, \underline{\lambda}_{ex}) = U_o + \langle \Phi_{ex} | H_p | \Phi_{ex} \rangle_o + V_L(\underline{o}) + \tfrac{1}{2} \underline{F}_{o ex} \cdot \underline{\xi}_{ex}$$

and $$E'_g(\underline{\xi}_{ex}, \underline{\lambda}'_g) = U_o + \tfrac{1}{2} \underline{\xi}_{ex} \cdot \underline{\underline{A}} \cdot \underline{\xi}_{ex} + V_L(\underline{\xi}_{ex}) + \langle \Phi'_g | H_p | \Phi'_g \rangle' \quad (43)$$

where Φ'_g = the pseudo wave function of the unrelaxed F-centre ground state.

Again from equation (27) one can obtain an expression for $\underline{\xi}_{ex} \cdot \underline{\underline{A}} \cdot \underline{\xi}_{ex}$

$$\underline{\xi}_{ex} \cdot \underline{\underline{A}} \cdot \underline{\xi}_{ex} = -\underline{F}_{o ex} \cdot \underline{\xi}_{ex} - \underline{\xi}_{ex} \cdot \underline{\underline{F}}'_{ex} \cdot \underline{\xi}_{ex} + \underline{\xi}_{ex} \cdot \underline{\underline{\Lambda}}_{ex} \cdot (\underline{\underline{\Lambda}}'_{ex})^{-1} \cdot \underline{\underline{\Lambda}}_{ex} \cdot \underline{\xi}_{ex}$$

and hence

$$E_{em}(\underline{\xi}_{ex}, \underline{\lambda}_{ex}, \underline{\lambda}'_g) = \left[\langle \Phi_{ex}|H_p|\Phi_{ex}\rangle_0 - \langle \Phi'_g|H_p|\Phi'_g\rangle'\right] + \left[V_L(\underline{0}) - V_L(\underline{\xi}_{ex})\right] + \left[\underline{F}_{0ex}\cdot\underline{\xi}_{ex} + \frac{1}{2}\underline{\xi}_{ex}\cdot\underline{\underline{F}}'_{ex}\cdot\underline{\xi}_{ex} - \frac{1}{2}\underline{\xi}_{ex}\cdot\underline{\underline{\Lambda}}_{ex}\cdot(\underline{\underline{\Lambda}}'_{ex})^{-1}\cdot\underline{\underline{\Lambda}}_{ex}\cdot\underline{\xi}_{ex}\right] \quad (44)$$

2.3 SHELL MODEL OF IONS

I shall first give a brief historical background to the treatment of ionic polarization in crystal lattice calculations. Many of the properties of alkali halide crystals such as cohesive energy and elastic constants are explained quite well on the basis of a model which assumes the ions to be fully ionized and unpolarized and considers the forces between ions to be electrostatic forces between point charges plus a short range repulsive force between closed electron shells. On the basis of this model Kellerman[14] calculated dispersion curves for NaCl. That is he considered the Born-von Kármán theory of lattice dynamics which describes the motion of the nuclei, in the harmonic approximation, by an effective potential which depends only on the nuclear co-ordinates and describes the electrons in the adiabatic approximation. Kellerman was able to account satisfactorily for the measured elastic constants, the infrared absorption frequency, and the variation of the Debye Θ with temperature as deduced from specific heat measurements. However, when Woods *et al* compared[15] calculations based on this Born model with experimental quantities such as dispersion curves which are more sensitive to the model they found strong disagreement with experiment. Also when the rigid ion model was used to fit the experimental data for germanium it was necessary to introduce short range interactions out to fifth nearest neighbours. However, this involves fifteen arbitrary and independent

constants so that the fit loses most of its physical significance.[16]

Furthermore, since the Born model treats the ions as point charges with zero polarizability the theory predicts that the high frequency dielectric constant, ϵ_∞, be 1 while in fact ϵ_∞ is 2.25 for NaCl. To account for the dielectric properties of the crystal Lyddane and Herzfeld[17] allowed the ions to be polarized by introducing polarizabilities $\alpha_\pm$ for the positive and negative ions in the crystal. On the basis of this model they calculated dispersion curves but their agreement with experiment was worse than that obtained by Kellerman.

The difficulties of the rigid ion model can be resolved by the introduction of the concept of distortion polarization.[18,19] This was introduced to explain why it was necessary to define an effective charge and compressibility in order to satisfy the Szigeti relationships which involve only experimental parameters, and which were derived on the basis of the Born model, where polarization is accounted for by the introduction of a polarizability for each ion, in the Lorentz field approximation. This distortion polarization is in addition to that considered by Szigeti and is due to the change in overlap forces between ions when the electron clouds of the ions are distorted by an external electric field.

Dick and Overhauser[20] have shown that the distortion polarization of an ion which results from the overlap forces

may be approximately represented by a mechanical model in which the ion consists of a core and a spherically symmetric shell. This shell may be relatively displaced from the core by either the local field or the overlap forces, thus producing both field polarization and distortion polarization of the ion. It is further assumed that the shell remains spherically symmetric when it is displaced relative to the core. The core and shell are assumed to be coupled by an isotropic force constant and the short range forces are assumed to act between the shells (fig. 4). The shell model in this form doubles the number of degrees of freedom of each ion. That is the displacement and polarization of an ion is described by six co-ordinates, three co-ordinates giving the displacement of the ion core plus three co-ordinates giving the displacements of the outer electron shells.

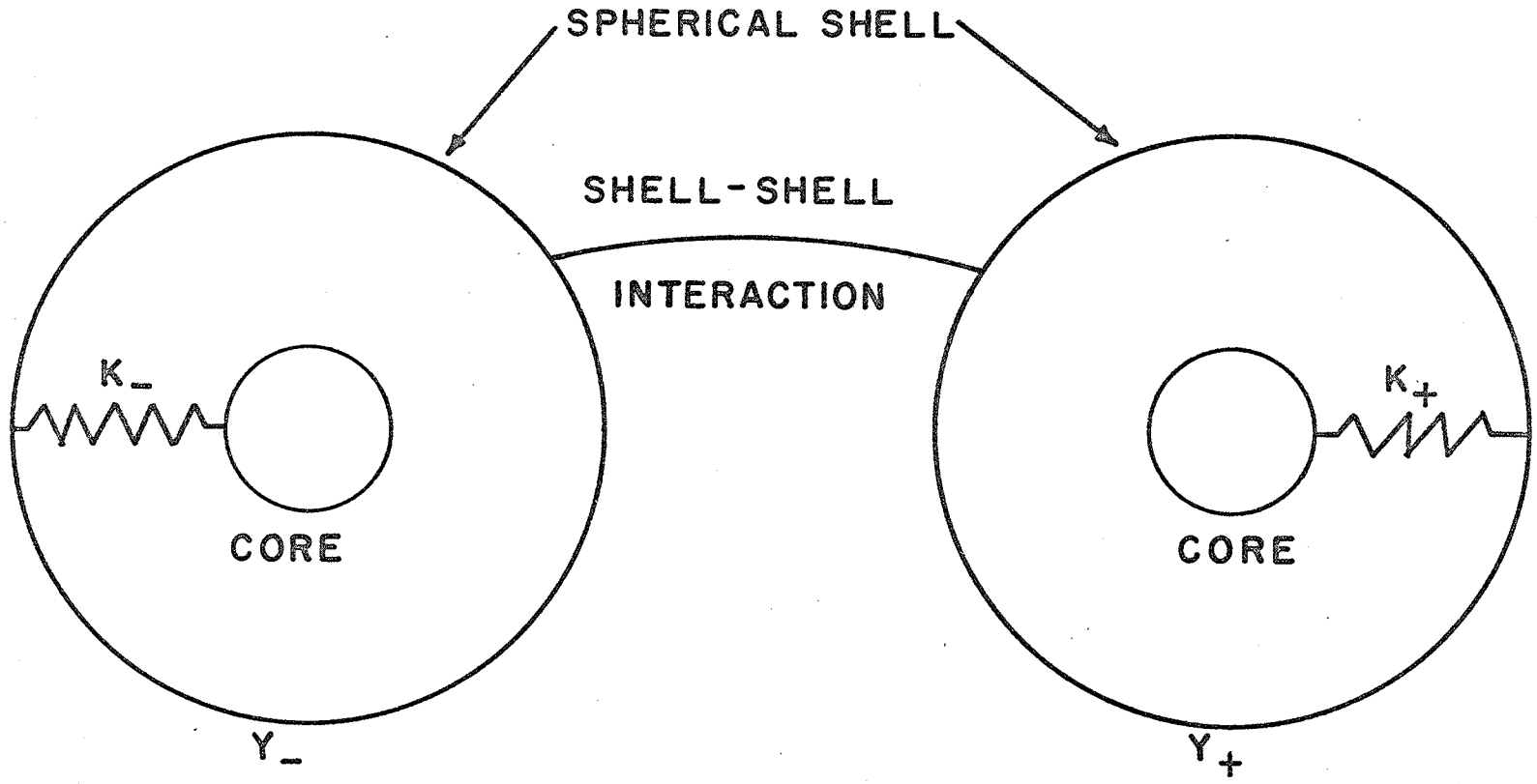
In lattice calculations based on this model the harmonic approximation is retained and the equivalent of the adiabatic approximation is achieved by assuming that the mass of the electron shells is negligible (that is the shells occupy positions of equilibrium at all times).

A generalization of this shell model is presented by Cochran.[21,22,23]

In the earliest work by Kellerman only three experimental quantities were required to fit the parameters which arise in setting up the dynamical matrix. These are the compressibility, the lattice parameter, and the ionic charge.

FIGURE 4.

Shell model representation of an ion pair. The cores are coupled to the shells by a spring of force constant $k_{\pm}$ for ($\pm$) ions. $Y_{\pm}$ are the number of electrons on the outer spherical shells for ($\pm$) ions.


SPHERICAL SHELL
SHELL-SHELL
INTERACTION
K_
CORE
Y_
K+
CORE
Y+

However when one considers a shell model for the ions there are further parameters which must be fixed from experimental data. These are the charges on the shells of the anions and cations and the force constants for the anions and cations which specify the interaction between the core and the shell of the ion. These added parameters may be determined from the static and high frequency dielectric constants, the infrared absorption frequency, and the free ion polarizabilities. Expressions for these parameters in terms of the experimental quantities is given by Havinga.[24] If other than nearest neighbour short range interactions are considered one may fit the added parameters by using the elastic constants. Expressions for these elastic parameters in terms of the shell model parameter are given by Cowley.[25]

Some work was done on extending the calculation of the present work to include electronic polarization but the results appear suspect so they will not be reported. This section is added mainly as a guide for extending the present work to account for electronic polarization.

CHAPTER III

CALCULATIONS, RESULTS AND DISCUSSION

3.1 F-CENTRE

A. ABSORPTION ENERGY

The F-centre was chosen as a starting point in the application of the method described in the previous section. As an aid in referring to the different states I shall refer to say the energy of the system when the F-centre electron is in its ground state as the energy of the F-centre ground state (a similar nomenclature will be used for the excited state).

In order to calculate the absorption energy of the F-centre it is necessary as a first step to locate the position of the relaxed ground state of the system. This is given by equation (26)

$$E_g(\underline{\xi}_g, \underline{\lambda}_g) = E_g(\underline{0}, \underline{\lambda}_{0g}) + \tfrac{1}{2} \underline{F}_{0g} \cdot \underline{\xi}_g$$

where
$$E_g(\underline{0}, \underline{\lambda}_{0g}) = U_0 + \langle \Phi_g | T | \Phi_g \rangle_0 + \langle \Phi_g | V_p | \Phi_g \rangle_0 + V_L(\underline{0}) \qquad (45)$$

Φ_g = the pseudo wave function for the ground state of the F-centre electron

T = the kinetic energy operator

V_p = the pseudopotential energy operator

and the $_0$ after the matrix element denotes that they are evaluated in an undistorted lattice containing a negative ion vacancy ($\underline{\xi}_g = \underline{0}$). From equation (16) we have that

$$\langle \Phi_g | V_p | \Phi_g \rangle_0 = \langle \Phi_g | V_{PI} | \Phi_g \rangle_0 + \sum_i C_i |\Phi_g(\vec{r}_i)|^2 \qquad (46)$$

The pseudo wave function Φ_g was chosen to be of the form $A r^{n} e^{-\alpha^2 r^2}$ where A is determined from the normalization condition and α is a localization parameter. Such a form for the pseudo wave function was chosen because:

(i) It is smooth which is one of the requirements of the pseudopotential method.

(ii) It is vacancy centred and hence would be expected to represent the charge distribution of the F-centre electron well.

(iii) It is spherically symmetric.

(iv) It is an easy form to handle in a calculation as all matrix elements involved may be either evaluated explicitly or represented as an error function which is easily evaluated by computer.

The determination of the energies involved in this problem require one to make extensive use of a computer since most of the expressions involved are quite lengthy and it would be foolish to attempt to calculate them by any other means. Part of this work was carried out at the University of St. Andrews, Scotland, the Atomic Energy Research Establishment (AERE) at Harwell, England, and the University of Manitoba. Consequently, four different types of computers were used. These were

(i) an IBM 360/65 at Harwell and Manitoba

(ii) an IBM 1620 at St. Andrews

(iii) an IBM 360/44 at St. Andrews

(iv) an Atlas computer which is made available

to persons at British universities if the available computing facilities are inadequate for the undertaking as was the case at St. Andrews before the IBM 360/44 became operational.

The first step in the calculation, namely to determine the relaxed ground state energy, involves the minimization of $E_g(\underline{o}, \underline{\lambda}_g)$ with respect to the parameter α (which stands for $\underline{\lambda}_g$ in this case) where $V_{PI}(\vec{r})$ is given by equation (A4) in appendix A and from equation (17)

$$\sum_i C_i |\Phi_g(\vec{r}_i)|^2 = \sum_i \left[A_i + B_i (\bar{V} - U_i) \right] |\Phi_g(\vec{r}_i)|^2$$

It is to be noted that this minimization involves an iterative procedure, since $\bar{V} = \langle \tilde{\Phi}_g | V_p | \tilde{\Phi}_g \rangle$, where $\tilde{\Phi}_g$ = the actual pseudo wave function for the ground state of the F-centre electron. To perform this self-consistent calculation one initially assumes a value for $\bar{V}$, completes the minimization procedure, recalculates $\bar{V}$ and compares it to the original estimate. If the two values did not agree to within .001 rydbergs, the minimization procedure was repeated using the new value of $\bar{V}$. This process is then repeated until one satisfies the convergence criterion, namely that two consecutive estimates of $\bar{V}$ differ by less than .001 rydbergs.

It should be recalled that the interaction between ions is between point charges with a repulsive interaction between nearest neighbour ions. However the interaction between the F-centre electron and the ions takes account of the finite size of the crystal ions by the last term in equation (46).

Thus in such a model

$$V_L(\underline{0}) = \sum_i \frac{Q_i}{r_i} - \sum_{mm}^{i} A'_{gl} e^{-r_i/\rho}$$

where $r_i \equiv |\vec{r}_i|$ and a Born-Mayer form for the repulsive interaction between nearest neighbours was chosen (the second sum is over nearest neighbour ions to the F-centre while the first sum is over all ions of the crystal). Since this expression for $V_L(\underline{0})$ does not involve α it does not affect the first minimization procedure with respect to α, but it does have an effect on the lattice distortion.

This minimization with respect to α was performed by a subroutine supplied by AERE, Harwell. The results are given in table 1. The value of the standard deviation σ, for a normal distribution of the form $A_l e^{-\alpha^2 r^2}$ corresponds to the position where the wave function has decreased to .606 of its central value of A and hence the probability density $|A_l e^{-\alpha^2 r^2}|^2$ has decreased to .369 of its central value of $|A|^2$ The standard deviation is related to the localization parameter α by

$$\sigma = \frac{1}{\sqrt{2}\,\alpha}$$

For the nine crystals considered, one can see from table 1 that the standard deviation is about .62 of the interionic spacing. As an example, for NaCl, the value of $|\Phi_g(\vec{r})|^2$ at the position of the first nearest neighbour ions to the defect is .074 $|A|^2$. Hence it is seen that the wave function for the ground state of the F-centre electron is well localized within the vacancy in the zeroth order approximation, in

TABLE 1. F-CENTRE GROUND STATE (ZEROTH ORDER CALCULATION)

crystal	NaCl	KCl	NaBr	KBr
point ion contr. (V_{PI})	-.609	-.544	-.574	-.518
ion size contr. (I.S)	.023	.003	.017	.003
$\frac{I.S.}{\lvert V_{PI}\rvert} \times 100$	3.8%	.6%	3.0%	.6%
$\langle \Phi_g \lvert V_P \rvert \Phi_g \rangle_o$	-.587	-.541	-.556	-.515
$\langle \Phi_g \lvert T \rvert \Phi_g \rangle_o$	.137	.107	.121	.097
alpha	1.14	1.12	1.13	1.12
$\langle \Phi_g \lvert H_P \rvert \Phi_g \rangle_o$	-.449	-.433	-.436	-.417

All energies are in rydbergs and alpha has units of reciprocal interionic spacing.

TABLE 1. continued

crystal	NaI	KI	LiCl	LiBr	LiI
point ion contr. (V_{PI})	-.536	-.491	-.664	-.620	-.575
ion size cont. (I.S.)	.016	.007	.030	.022	.020
$\frac{I.S.}{\lvert V_{PI}\rvert} \times 100$	3.0%	1.3%	4.5%	3.5%	3.5%
$\langle \Phi_g \lvert V_P \rvert \Phi_g \rangle_o$	-.521	-.484	-.634	-.598	-.555
$\langle \Phi_g \lvert T \rvert \Phi_g \rangle_o$	.109	.091	.161	.139	.124
alpha	1.17	1.16	1.13	1.12	1.15
$\langle \Phi_g \lvert H_P \rvert \Phi_g \rangle_o$	-.411	-.393	-.473	-.459	-.431

All energies are in rydbergs and alpha has units of reciprocal interionic spacing.

agreement with other theoretical work on the F-centre ground state.[26-30] Furthermore the ion-size contribution to the interaction energy between the F-centre electron and the ions is positive, compared to a negative interaction energy when the ions are considered to be point ions. Also, the percentage of this contribution compared to the point ion contribution ranges from about .6% for the potassium halides to 4.5% for LiCl.

It should also be noted that $\langle \Phi_g | T | \Phi_g \rangle$ is small compared to $\langle \Phi_g | V_p | \Phi_g \rangle$ which is to be expected since Φ_g was chosen to be a smooth pseudo wave function.

The next step in the procedure to determine the relaxed ground state energy of the system is to allow the lattice to relax. Although the zeroth order calculation was carried out for nine crystals the relaxed energy was computed for only two crystals, NaCl and KCl.

As a first approximation it is assumed that electronic polarization effects may be neglected, and hence the calculation of the relaxation involves only the determination of the displacements of the ions. This is most likely a good approximation for a localized state but may not be so for a more diffuse state[27,29]. However the calculations of Gourary and Adrian indicate that polarization effects for an F-centre electron in its ground and excited states are small.[26]

In order to calculate the displacements of the ions

surrounding the defect consider equation (28). From this equation one may calculate the fourier transform, $\underline{Q}(\vec{q})$, of the displacements, $\underline{\xi}$, for each $\vec{q}$ vector, provided $D_{\alpha\beta}^{KK'}(\vec{q})$ is known. These $D_{\alpha\beta}^{KK'}(\vec{q})$ have been evaluated by Kellerman,[14] (a correction to this calculation is given by Dayal and Tripathi[31]), for 1000 $\vec{q}$ vectors in the Brillouin zone for a NaCl-type lattice. The choice of 1000 $\vec{q}$ vectors means that one is in effect choosing a crystal which contains only 1000 unit cells.

The dynamical matrices, $D_{\alpha\beta}^{KK'}(\vec{q})$, which are involved are 6×6 corresponding to the values 1,2,3 which α and β may assume and the values 1,2 which K and K' may assume. The α and β refer to the three possible components of displacement while the K and K' refer to the two ions per unit cell.

When setting up the dynamical matrix it is possible to separate the coulomb and short range contributions. One need not specify the form of the short range interaction as it is only necessary to know the first and second derivatives of the interaction which are evaluated from the compressibility and the equilibrium lattice spacing. For the F-centre ground state, which we have taken to be spherically symmetric, contributions to the calculation from first, second, third and fourth nearest neighbours were considered. That is, in equation (36) the summation was extended out to fourth nearest neighbours and the displacements were calculated out to fifteenth nearest neighbours. The largest displacements were

for the nearest neighbour ions and in the calculation of $\underline{F}_{0g} \cdot \underline{\xi}_g$ these ions contributed the largest amount. In appendix B I show how the ions are grouped for this calculation and give the explicit form for $\underline{G}(\vec{q})$ for each group.

Table 2 gives the displacements of the ions for the ground states of the F-centre for NaCl and KCl. It is seen that these displacements are quite small even for the nearest neighbours to the F-centre and in towards the F-centre. This is to be expected since for a compact Φ_g the F-centre electron charge is nearly all within the vacancy. Consequently, the change in the coulomb interaction when an anion is removed and replaced by an electron would be expected to be small and the main result of the substitution would be to remove the ion-ion nearest neighbour repulsive interaction between the missing anion and the six adjacent cations and replace it by an interaction which takes into account the finite size of the ions in the crystal for the F-centre electron-ion interaction. Since the ion size interaction energy is smaller than the repulsive nearest neighbour interaction it seems reasonable that an inward displacement of the ions would result. Also, there is close agreement between the magnitudes of the displacements in both crystals.

Table 3 shows the corrections to the ground state energy of the system referred to a zero corresponding to the energy of a perfect undistorted lattice (U_o). This calculation was performed considering two different forms for the nearest

TABLE 2. DISPLACEMENT OF IONS: F-CENTRE GROUND STATE

	NaCl			KCl		
ion	x	y	z	x	y	z
(100)	-0.026	0.000	0.000	-0.025	0.000	0.000
(110)	-0.012	-0.012	0.000	-0.013	-0.013	0.000
(111)	0.001	0.001	0.001	0.002	0.002	0.002
(200)	-0.011	0.000	0.000	-0.017	0.000	0.000
(210)	-0.007	-0.005	0.000	-0.007	-0.004	0.000
(211)	-0.002	-0.000	0.000	-0.002	0.000	0.000
(220)	-0.004	-0.004	0.000	-0.004	-0.004	0.000
(221)	-0.001	-0.001	0.000	0.000	0.000	0.000
(300)	-0.004	0.000	0.000	-0.009	0.000	0.000
(310)	-0.004	-0.001	0.000	-0.005	-0.002	0.000
(311)	-0.002	-0.001	-0.001	-0.003	0.000	0.000
(222)	-0.000	-0.000	0.000	0.000	0.000	0.000
(320)	-0.002	-0.002	0.000	-0.003	-0.002	0.000
(321)	-0.001	-0.001	0.000	-0.001	0.000	0.000
(400)	-0.002	0.000	0.000	-0.004	-0.000	0.000

All displacements are in units of the interionic distance and the negative direction is inward toward the vacancy.
The repulsive nn interaction was the Born-Mayer form.

TABLE 3. RELAXED ENERGY FOR F-CENTRE ELECTRON IN THE GROUND STATE

	crystal			
	NaCl		KCl	
	Born-Mayer	inverse power	Born-Mayer	inverse power
$V_L(\underline{o})$ coulomb	.656	.656	.590	.590
$V_L(\underline{o})$ repulsive	-.075	-.086	-.062	-.068
$\frac{1}{2}\underline{F}_{og}\cdot\underline{\xi}_g$	-.003	-.003	-.004	-.004
$\langle\Phi_g\|H_p\|\Phi_g\rangle_o$	-.449	-.449	-.433	-.433
$E_g(\underline{o},\underline{\lambda}_{og})-U_o$	.132	.121	.095	.089
$E_g(\underline{\xi}_g,\underline{\lambda}_g)-U_o$	.129	.118	.091	.085
% relaxation	2.3%	2.5%	4.4%	4.7%

All energies in rydbergs.

Calculation for two forms of the repulsive interaction.

neighbour repulsive interaction, namely a Born-Mayer exponential form $(A_1 e^{-r/\rho})$ and an inverse power form (A_2/r^n). The calculated displacements and energy changes were almost exactly the same. However, this is to be expected since one determines the two parameters (A_1 and ρ in the first case and A_2 and n in the second case) by the requirement that $\left[\frac{\partial U}{\partial r}\right]_{r=a} = 0$ and $\frac{1}{K} = V\left[\frac{\partial^2 U}{\partial r^2}\right]_{r=a}$.

where U = the energy of the crystal

K = the compressibility

V = the volume of the crystal

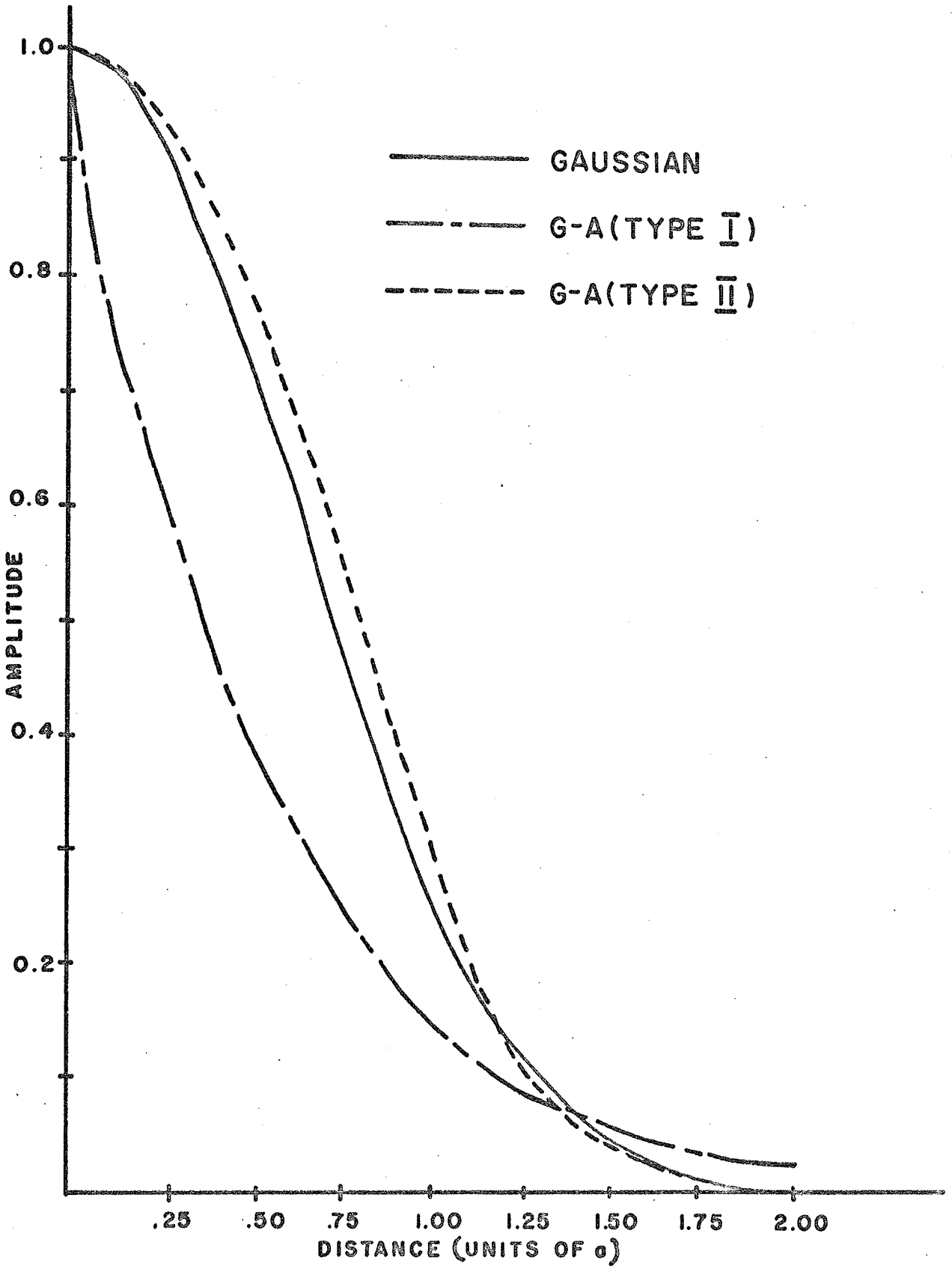
and a = the interionic separation.

That is, one is determining the two parameters in both cases by requiring that their first and second derivatives be equal to the same quantities at r = a . But in the determination of the displacements only these derivatives of the repulsive interaction are used, hence one expects the same result.

Figure 5 shows a comparison of my ground state pseudo wave function Φ_g and those considered by Gourary and Adrian[26] for NaCl. It is seen that at a distance of one interionic spacing (a) from the anion vacancy Φ_g has decreased to .26 of its central value and is negligibly small at a distance of 2a from the origin (which is the centre of the anion vacancy). The Gourary-Adrian type I wave function decreased to a value of .15 of its central value at r = a while the type II and type III decreased to a value of .27 of their central value at this same distance. Furthermore all three

FIGURE 5.

Ground state F-centre wave function for NaCl. Distance is measured from the centre of the anion vacancy. The Gourary-Adrian (G-A) type II and type III are very similar so only the type II was plotted. a is the bulk equilibrium interionic spacing.


1.0
0.8
0.6
0.4
0.2
AMPLITUDE
GAUSSIAN
G-A(TYPE I)
G-A(TYPE II)
.25
.50
.75
1.00
1.25
1.50
1.75
2.00
DISTANCE (UNITS OF σ)

types were negligibly small at r = 2a. Although Gourary and Adrian do not explicitly mention it their wave functions are in effect pseudo wave functions since they are smooth and not orthogonalized to the core orbitals. Since the pseudo wave function that arises from the calculation is compact there is some justification for using the adiabatic approximation, for it is believed that electrons in compact states move so rapidly that the ions can not follow the motion and see the average electron distribution. Furthermore, since the pseudo wave function is compact one feels justified in neglecting electronic polarization, at least for distant ions to the defect since they see a neutral defect.

The next step in the calculation of the absorption energy is to calculate the unrelaxed excited state energy $E'_{ex}(\underline{\xi}_g, \underline{\lambda}'_{ex})$ from equation (39). First $\langle \Phi'_{ex} | H_p | \Phi'_{ex} \rangle'$ was evaluated in the presence of the F-centre ground state distortion where $\Phi'_{ex} = A\, e^{-\alpha^2 r^2} r \cos\theta$ and α was the variational parameter. Again this evaluation involved the minimization of

$$E'_{ex}(\underline{\xi}_g, \underline{\lambda}'_{ex}) = U_0 + \tfrac{1}{2}\, \underline{\xi}_g \cdot \underline{\underline{A}} \cdot \underline{\xi}_g + \langle \Phi'_{ex} | T | \Phi'_{ex} \rangle'$$

$$+ \langle \Phi'_{ex} | V_{PI} | \Phi'_{ex} \rangle' + \sum_i{}' C_i \, |\Phi'_{ex}(\vec{r}_i)|^2 + V_L(\underline{\xi}_g)$$

with respect to α accompanied by an iterative procedure to calculate $\bar{V} = \langle \tilde{\Phi}'_{ex} | V_p | \tilde{\Phi}'_{ex} \rangle$ where $\tilde{\Phi}'_{ex}$ is the actual wave function for the F-centre electron in the excited state (in the presence of the distortion field $\underline{\xi}_g$ of the ground state F-centre). $V_L(\underline{\xi}_g)$ is the change that results when an

anion is removed from the crystal in the presence of the distortion field $\underline{\xi}_g$. The expression for $V_{PI}(\vec{r})$ for such a wave function is given by equation (A6) in appendix A. The results of this minimization procedure are given in table 4 and the absorption energies (using equation (42)) are also given in this table. It is seen that the absorption energies agree quite well with experiment. This is not surprising since the absorption of F-centres in alkali halides was one of the experimental parameters used by Bartram et al[9] in the determination of the semi-empirical pseudopotential ion size coefficients. It does indicate, however, that a Gaussian fits the F-centre energy about as well as a Gourary-Adrian type of wave function.

B. EMISSION ENERGY

The calculation of the emission energy follows the same lines as that for the absorption energy. The first step is to find the energy of the relaxed system when the F-centre electron is in its first excited state Φ_{ex}. It is important to be able to locate this level accurately because the activation energy for F-centre step diffusion depends on it.[32] That is, it is supposed that an F-centre electron goes through the anti-symmetric state of the saddle-point configuration when step-diffusion occurs, and hence the difference in energy of the system between the anti-symmetric saddle-point and the relaxed excited F-centre will furnish an estimate of the activation energy for step diffusion.

TABLE 4. F-CENTRE ABSORPTION ENERGIES

	crystal	NaCl	KCl
$V_L(\underline{\xi}_g)$	coul	.679	.601
	repul.	-.094	-.082
$\frac{1}{2}\underline{F}_{0g}\cdot\underline{\xi}_g$		-.003	-.004
$\frac{1}{2}\underline{\xi}_g\cdot\underline{F}'_g\cdot\underline{\xi}_g$		-.001	-.001
$\frac{1}{2}\underline{\xi}_g\cdot\underline{\Lambda}_g\cdot(\underline{\Lambda}'_g)^{-1}\cdot\underline{\Lambda}_g\cdot\underline{\xi}_g$		.000	.000
$\langle\Phi'_{\omega}\lvert H_p\rvert\Phi'_{\omega}\rangle'$		-.252	-.267
$E'_{\omega}(\underline{\xi}_g,\underline{\lambda}'_{\omega})-U_0$		.337	.258
$E_g(\underline{\xi}_g,\underline{\lambda}_g)-U_0$		.129	.091
$E'_{\omega}-E_g$		.208	.167
exp. absorption en.		.204*	.170*

All energies are in rydbergs.

A Born-Mayer form for the repulsive interaction was used.

*The experimental values are taken from reference 4.

As before one minimizes $\langle \Phi_{sw} | H_p | \Phi_{sw} \rangle_o + V_L(\underline{o})$ with respect to the wave function parameters. The pseudo wave function was chosen to be of the form $A_N \cos\theta e^{-\alpha^2 N^2}$. The results of the minimization procedure are shown in table 5.

To calculate the relaxation of the excited state one proceeds to calculate the displacements, as before, using equation (37). The main difference in the calculation from the F-centre ground state is that we no longer have spherical symmetry and consequently the grouping of the ions in equation (36) is different corresponding to the changed symmetry. The manner in which the ions are grouped is shown in appendix B. Equation (B7) to (B13) give the contributions to $\underline{G}(\vec{q})$ from each group. The displacements of ions out to tenth nearest neighbours were calculated, considering the contributions to equation (36) from ions out to and including those at (200) and (002). These displacements are shown in table 6. It can be seen that the displacements of the (100) ions are quite large and outward from the vacancy. This is in qualitative agreement with the calculation of Wood and Joy.[27] However, they also found a large outward displacement for the (001) ions compared to my values of .002a for NaCl and -.021a for KCl (the negative sign denotes an inward displacement). For NaCl Wood and Joy found displacements of .0898a and .1297a for the (100) and (001) ions respectively.

Figure 6 shows a graph of the F-centre excited state pseudo wave function. This is compact, peaking at about .6a. Gourary and Adrian[26] found that their type I function peaked

TABLE 5. ENERGY LEVELS FOR F-CENTRE EXCITED STATE

crystal	NaCl		KCl	
	Born-Mayer	inverse power	Born-Mayer	inverse power
$V_L(\underline{0})$ coul	.656	.656	.590	.590
$V_L(\underline{0})$ repul.	-.075	-.086	-.062	-.068
point ion cont. (V_{PI})	-.547	-.547	-.490	-.490
ion size cont. (I.S.)	.048	.048	.015	.015
$\frac{\text{I.S.}}{\lvert V_{PI}\rvert} \times 100$	8.8%	8.8%	3.1%	3.1%
$\bar{V}$	-.499	-.499	-.475	-.475
$\langle \Phi_{\mu} \lvert T \rvert \Phi_{\mu} \rangle_0$	.251	.251	.202	.202
α_0	1.19	1.19	1.19	1.19
$\langle \Phi_{\mu} \lvert H_p \rvert \Phi_{\mu} \rangle_0$	-.248	-.248	-.273	-.273
$E_{\mu}(\underline{0}, \underline{\lambda}_{0\mu}) - U_0$	.333	.322	.254	.248
$\frac{1}{2} \underline{F}_{0\mu} \cdot \underline{\xi}_{\mu}$	-.021	-.021	-.017	-.017
corrected alpha	1.10	1.10	1.12	1.12
$E_{\mu}(\underline{\xi}_{\mu}, \underline{\lambda}_{\mu}) - U_0$	.311	.301	.237	.231
% relaxation	6.3%	6.5%	6.7%	6.8%

All energies are in rydbergs.

$\alpha_0 \sim \underline{\lambda}_{0\mu}$ (from zeroth order energy calculation)

Calculation for two forms of the repulsive interaction.

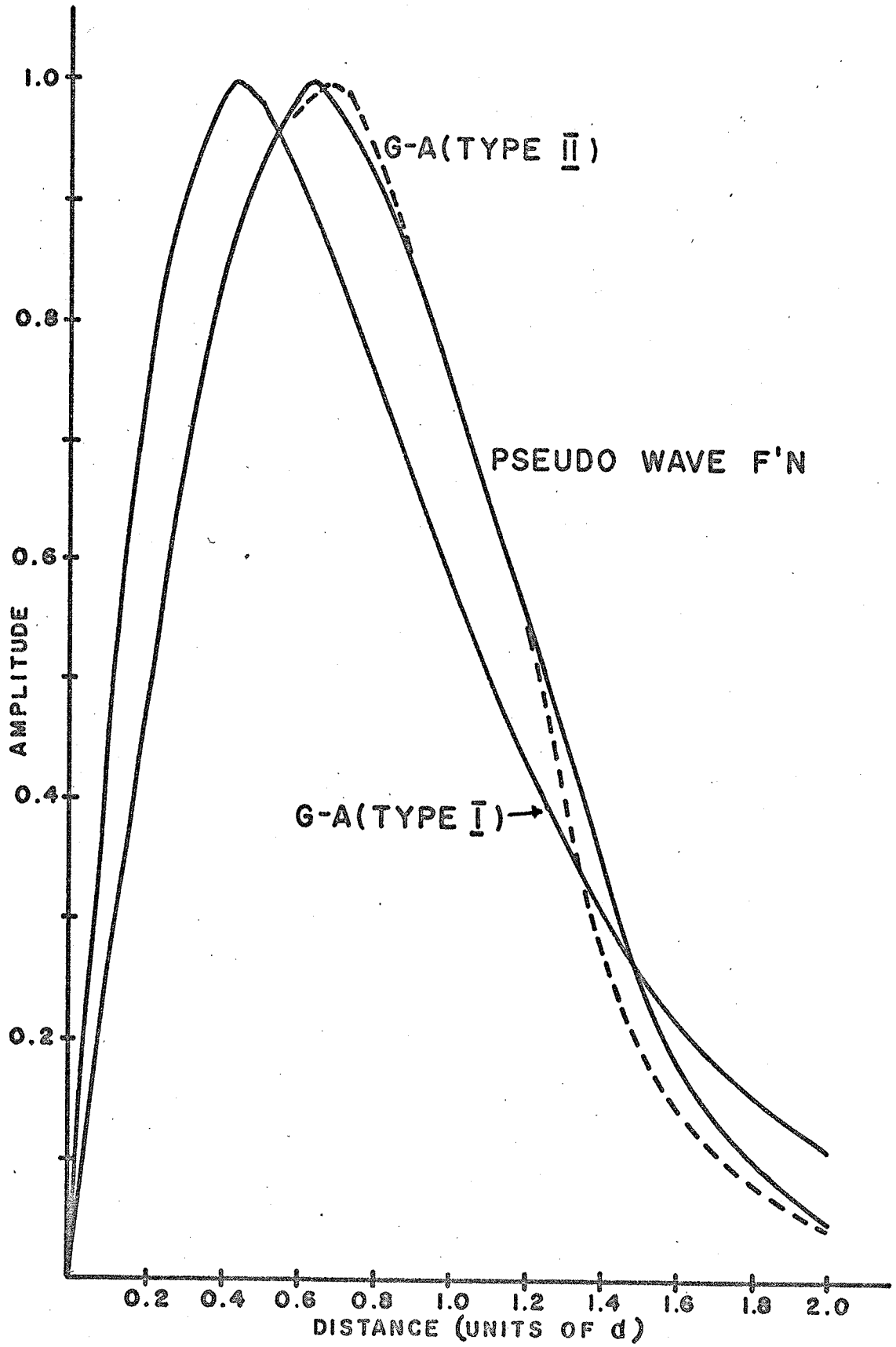
TABLE 6. DISPLACEMENT OF IONS: F-CENTRE EXCITED STATE

	crystal					
	NaCl			KCl		
ion	x	y	z	x	y	z
100	.081	.000	.000	.058	.000	.000
001	.000	.000	.002	.000	.000	-.021
110	.012	.012	.000	-.023	-.023	.000
101	.036	.000	-.007	.014	.000	-.016
111	.009	.009	.013	-0.000	.000	.008
200	.023	.000	.000	.006	.000	.000
002	.000	.000	.007	.000	.000	-.026
120	.002	.001	.000	-.002	-.008	.000
201	.012	.000	.004	.005	.000	.000
102	.006	.000	-.001	.000	.000	-.011
211	.006	.005	.001	.000	.001	.000
112	.001	.001	.002	.000	.000	.000
220	.000	.000	.000	-.004	-.004	.000
202	.005	.000	.003	.001	.000	-.002
221	.004	.004	.002	.001	.001	.001
212	.004	.001	.002	.001	.000	.000
300	.008	.000	.000	.002	.000	.000
003	.000	.000	-.001	.000	.000	-.013
310	.004	.002	.000	-.002	.000	.000
301	.007	.000	.003	.002	.000	.000
103	.002	.000	.000	-.001	.000	-.007
311	.004	.001	.000	.000	.000	-.001
113	.000	.000	.000	.000	.000	-.002

Displacements in units of the interionic spacing.
Positive direction is outward from the F-centre.

FIGURE 6.

Excited state F-centre wave function for NaCl. Distance is measured from the centre of the anion vacancy. The Gourary-Adrian (G-A) type II and type III are very similar so only the type II was plotted. a is the bulk equilibrium interionic spacing.


1.0
0.8
0.6
0.4
0.2
AMPLITUDE
G-A(TYPE II)
PSEUDO WAVE F'N
G-A(TYPE I)
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
DISTANCE (UNITS OF d)

at about .4a while their type II peaked at about .6a. This is in contrast to the results of W. Beall Fowler,[28] who uses a semi-continuum model, and obtains a diffuse wave function. However his calculation involves several parameters such as R, the radius of the potential well seen by the electron, m^*, the effective mass, and K_{eff}, an effective dielectric constant, which are fixed at values which would yield a diffuse wave function.

The next step is to calculate $E_g'(\underline{\xi}_{ex}, \underline{\lambda}_g')$ from equation (43). For such a calculation Φ_g' was chosen to be of the form $Ae^{-\alpha^2 r^2}$ (the same form as Φ_g). The results of this calculation and the emission energies are given in table 7.

One can see that the agreement with experiment for the emission energies is worse than for the absorption energies. One explanation of this may lie in the suggestion that the Franck-Condon principle does not hold in emission. If this were the case then the lattice would relax some from the configuration corresponding to the relaxed excited F-centre towards the configuration of the relaxed ground state F-centre during the emission, hence lowering the levels to which emission occurs. This would increase my emission energies and bring them nearer to the experimental values. Also electronic polarization effects have not been considered. They may be important in the F-centre excited state in view of the fact that the pseudo wave function Φ_{ex} peaks at approximately .6a and hence the probability that the F-centre electron will be very near the electrons of the neighbouring ions is

TABLE 7. F-CENTRE EMISSION ENERGIES

	crystal			
	NaCl		KCl	
	Born-Mayer	inverse power	Born-Mayer	inverse power
$V_L(\underline{\xi}_{\alpha\mu})$ coul	.656	.656	.590	.590
$V_L(\underline{\xi}_{\alpha\mu})$ repul	-.049	-.061	-.049	-.054
alpha for emission	1.10	1.10	1.11	1.11
$\langle \Phi'_g \lvert H_p \rvert \Phi'_g \rangle$	-.357	-.357	-.349	-.349
$\frac{1}{2} \underline{F}_{0\alpha\mu} \cdot \underline{\xi}_{\alpha\mu}$	-.021	-.021	-.017	-.017
$\frac{1}{2} \underline{\xi}_{\alpha\mu} \cdot \underline{F}'_{\alpha\mu} \cdot \underline{\xi}_{\alpha\mu}$	-.004	-.004	-.003	-.003
$\frac{1}{2} \underline{\xi}_{\alpha\mu} \cdot \underline{\Lambda}_{\alpha\mu} \cdot (\underline{\Lambda}'_{\alpha\mu})^{-1} \cdot \underline{\Lambda}_{\alpha\mu} \cdot \underline{\xi}_{\alpha\mu}$	.004	.004	.002	.002
$E'_g(\underline{\xi}_{\alpha\mu}, \underline{\lambda}'_g) - U_0$	.279	.267	.214	.209
$E_{\alpha\mu}(\underline{\xi}_{\alpha\mu}, \underline{\lambda}_{\alpha\mu}) - U_0$	.311	.301	.237	.231
emission en.	.032	.034	.023	.022
experimental emission en.	.072*	.072*	.089*	.089*

All energies in rydbergs.

* The experimental values are taken from reference 4 .

Calculation for two forms of the repulsive interaction.

very high. This could lead to polarization effects which are not negligible.

3.2 SADDLE POINT

In order to calculate the activation energy for step diffusion one must locate the energy of the system in the saddle-point configuration. In this saddle-point the system may exist in two possible quasi-static states, a symmetric and an antisymmetric, the antisymmetric being the higher in energy. The first step in the location of these energy levels is to calculate the zeroth order energy which does not take account of the relaxation of the lattice. That is one minimizes

$$E(\underline{o}, \underline{\lambda}_A^S) = U_o + \langle \Phi_A^S | H_p | \Phi_A^S \rangle_o + V_L(\underline{o})$$

$$E(\underline{o}, \underline{\lambda}_A^S) = U_o + \langle \Phi_A^S | T | \Phi_A^S \rangle_o + \langle \Phi_A^S | V_{PI} | \Phi_A^S \rangle_o + V_L(\underline{o}) + \sum_i C_i |\Phi_A^S(\vec{r}_i)|^2 \quad (47)$$

with respect to the wave function parameters, where Φ_S is the pseudo wave function of the symmetric state and Φ_A is the pseudo wave function for the antisymmetric state. Φ_A was chosen to be of the form $A_r \cos\theta\, e^{-\alpha^2 r^2} = A z\, e^{-\alpha^2 r^2}$ and Φ_S was chosen to be $A_r^2 \cos^2\theta\, e^{-\alpha^2 r^2} = A z^2 e^{-\alpha^2 r^2}$ where the co-ordinate system used was a defect orientated coordinate system (coordinate system labelled II in figure 1). These particular forms for Φ_S and Φ_A were chosen because they fit the charge distribution of the defect, namely they both have charge density lobes in the "half vacancies" straddling the saddle-point.

Note that $V_L(\underline{o})$ is now the change in lattice energy that results from extracting two anions from positions 2

and 3 of figure 1 and introducing an anion at position 4 when the distortion field is zero.

It was found that when equation (47) was minimized with respect to the wave function parameter and the ionic displacements were calculated, the displacement of the cations nearest the migrating anion (ions labelled by 1 in figure 1) were too large to be treated within the harmonic approximation of the Kanzaki method. Consequently this problem was considered as a two-parameter type of problem. That is, equation (47) was minimized with respect to the wave function parameter α and the positions of the nearest neighbour cations (group 1 ions) to the saddle-point anions. Thus, in equation (22) the positions of the group 1 ions were considered to be one component of $\underline{\lambda}$, rather than one component of $\underline{\xi}$. This also changes $V_L(\underline{o})$, since $V_L(\underline{o})$ must now take into account the fact that the group 1 ions have been displaced in minimizing equation (47). It was found that by allowing the group 1 ions to relax in such a manner that the equilibrium energy was substantially changed from the case where the group 1 ions were rigidly clamped at their perfect lattice sites. In other words the equilibrium energy is quite sensitive to the positions of the group 1 ions.

This minimization was carried out using a program from the library of subroutines at AERE, Harwell[33]. In order to calculate the energy expression given by equation (47) I used for $V_{pI}(\vec{r})$:

(i) equation (A7) from appendix A when considering Φ_A and (ii) equation (A8) from appendix A when considering $\Phi_s = A z^2 e^{-\alpha^2 r^2}$ since Φ_s may be written as a linear combination of $\ell = 0$ and $\ell = 2$ spherical harmonics, namely

$$\Phi_s = A e^{-\alpha^2 r^2} r^2 \left[P_2^0(\cos\theta) + \tfrac{1}{2} P_0^0(\cos\theta) \right]$$

A second form for Φ_s was also considered, namely $\Phi_s = A e^{-\alpha^2 r^2}(b^2 + z^2)$ to see if the resultant energy was much improved by including the parameter b. It was found that the initial minimization process gave almost the same zeroth order energy for both forms of Φ_s. It should be noted that for $\Phi_s = A e^{-\alpha^2 r^2}(b^2 + z^2)$ the minimization process now involves three parameters, α, b, and y_1, the y coordinate of the group 1 ions. Since these energies for the two different forms of Φ_s came out approximately the same further calculations involving the relaxation of the lattice were carried out only for the simplier form, namely $\Phi_s = A z^2 e^{-\alpha^2 r^2}$.

These calculations were performed using the two different forms, mentioned previously, for the short range repulsive interaction between ions. First a Born-Mayer form $\sim A_1 e^{-r/\rho}$ was used, but it was thought that for large deviations of the ions from their equilibrium spacing, perhaps a repulsive interaction of the form A_2/r^m would be more suitable. In both cases the values used for the constants (A_1, ρ) or (A_2, m) were those derived from bulk macroscopic data. There is no justification in using these values when the spacing between ions differs greatly from the equilibrium spacing.[34]

Some work is presently being done on the correction of these parameters using experimental results for the activation energy for diffusion of anion vacancies in alkali halide crystals. The results of this zeroth order energy calculation are shown in tables 8 and 9.

It can be seen from these tables that y_1, in the zeroth order approximation, is approximately the same, equal to about .85a. This is a displacement of about .14a from the value it would have if the group 1 ions were not allowed to move in this first minimization, or a displacement of about 20%.

One now allows the ions surrounding the saddle-point to relax. This is carried out as before by the Kanzaki method. The coordinate system that one must use for this calculation is that labelled by I in figure 1 and then one must perform the appropriate rotation to give the displacements in the defect orientated coordinate system. In doing this relaxation calculation, 40 groups of ions were allowed to relax about the defect. This includes relaxation out to fourteenth nearest neighbours to the defect or about 214 ions. In equation (36) the sum over ℓ included 12 groups of ions (included eight nearest neighbours to the defect or 54 ions). The order of the grouping of the ions and the subsequent contribution to $\underline{G}(\vec{q})$ from each group are shown in appendix B. The results of this calculation, the relaxed energy levels and the corrected variational parameters are shown in tables 8 and 9.

TABLE 8. SADDLE-POINT ENERGY LEVELS FOR NaCl

symmetry	antisymmetric		symmetric	
pseudo wave function	$\Phi_A = A_3 e^{-\alpha^2 n^2}$		$\Phi_S = A_3^2 e^{-\alpha^2 n^2}$	
form of rep. int.	Born-Mayer	inverse power	Born-Mayer	inverse power
point ion cont. (V_{PI})	-.385	-.383	-.437	-.435
ion size cont. (I.S.)	.051	.052	.042	.043
$\frac{\text{I.S.}}{\lvert V_{PI}\rvert} \times 100$	13.2%	13.6%	9.6%	9.9%
α_0	.833	.831	.978	.977
y_{10}	.829	.839	.832	.841
$\langle \Phi \lvert V_p \rvert \Phi \rangle_0$	-.334	-.331	-.395	-.392
kinetic energy	.122	.122	.146	.146
$\langle \Phi \lvert H_p \rvert \Phi \rangle_0$	-.212	-.210	-.249	-.247
$E(\underline{0}, \underline{\lambda}_0) - U_0$	.361	.364	.324	.326
$\frac{1}{2} \underline{F}_0 \cdot \underline{\xi}$	-.042	-.041	-.023	-.014
corrected α	1.02	1.06	1.00	1.01
corrected y_1	.816	.825	.831	.840
relaxed energy	.319	.323	.301	.312

All energies are in rydbergs.

$\alpha_0, y_{10} \sim \underline{\lambda}_0$ (from zeroth order energy calculation)

TABLE 9. SADDLE-POINT ENERGIES (KCl)

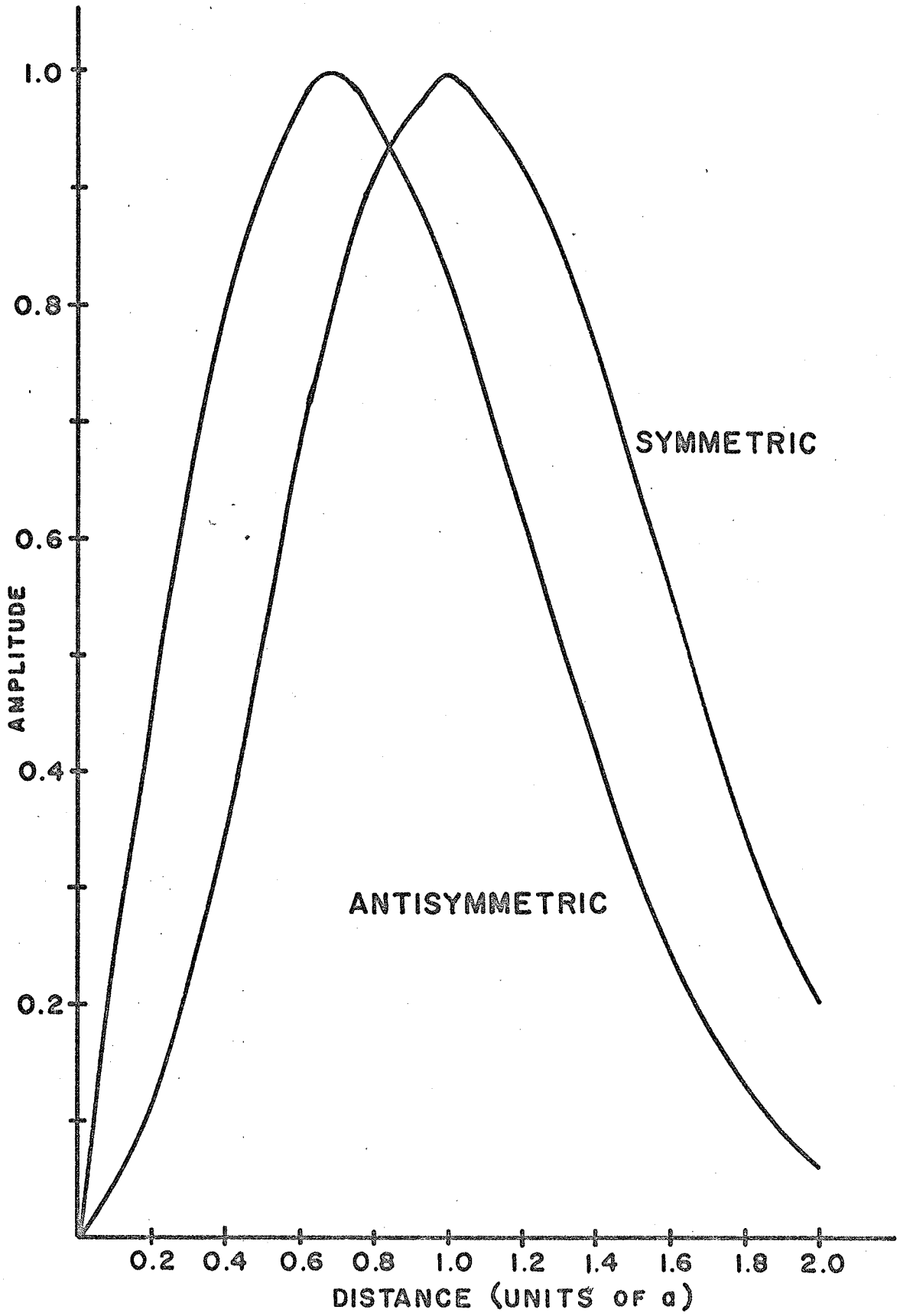
symmetry	antisymmetric		symmetric			
pseudo wave function	$\Phi_A = A z\, e^{-\alpha^2 r^2}$		$\Phi_s = A z^2 e^{-\alpha^2 r^2}$		$\Phi_s = A(b^2 + z^2) e^{-\alpha^2 r^2}$	
repulsive interaction	Born-Mayer	inverse power	Born-Mayer	inverse power	Born-Mayer	inverse power
point ion cont. (V_{PI})	-.339	-.338	-.386	-.385	-.362	-.360
ion size cont. (I.S)	.027	.028	.018	.018	.014	.014
$\frac{\text{I.S.}}{\lvert V_{PI}\rvert} \times 100$	8.0%	8.3%	4.7%	4.7%	3.9%	3.9%
α_0	.810	.810	.961	.960	.940	.939
b_0	-	-	-	-	.491	.492
y_{10}	.845	.850	.847	.852	.844	.850
$\langle \Phi \lvert V_p \rvert \Phi \rangle$	-.312	-.310	-.368	-.367	-.348	-.346
kinetic energy	.093	.093	.114	.114	.085	.084
$\langle \Phi \lvert H_p \rvert \Phi \rangle_0$	-.218	-.217	-.249	-.247	-.262	-.261
$E(\underline{\Omega}, \underline{\Delta}_0) - U_0$	.314	.315	.277	.278	.270	.271
$\frac{1}{2} \underline{F}_0 \cdot \underline{\delta}$	-.038	-.037	-.022	-.023	-	-
corrected alpha	1.04	1.04	.986	.991	-	-
corrected y_1	.832	.827	.846	.848	-	-
relaxed energy	.276	.278	.255	.255	-	-

All energies are in rydbergs.

$\alpha_0, b_0, y_{10} \sim \underline{\lambda}_0$ (from zeroth order energy calculation)

FIGURE 7.

Symmetric and antisymmetric saddle-point wave functions for NaCl. Distance measured from position of migrating anion at the saddle-point. a is the bulk equilibrium interionic spacing.


1.0
0.8
0.6
0.4
0.2
AMPLITUDE
SYMMETRIC
ANTISYMMETRIC
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
DISTANCE (UNITS OF a)

It can be seen that the relaxation of the antisymmetric state is considerably more than the relaxation of the symmetric state. Figure 7 shows a plot of the two pseudo wave functions $\Phi_S = A_3 z^2 e^{-\alpha^2 r^2}$ and $\Phi_A = A_3 z e^{-\alpha^2 r^2}$. It can be seen that the Φ_A peaks at about .7a while Φ_S peaks at about a. That is the symmetric pseudo wave function tends to locate the electron's charge more in the "half vacancies," while the antisymmetric pseudo wave function tends to move the electronic charge nearer the migrating anion.

The displacement field that is associated with these relaxations conforms to this picture as the two fields (for the symmetric and antisymmetric state) are qualitatively the same but the displacements associated with the antisymmetric state are larger.

Figures 8-11 show the energy level diagrams for two crystals considered in detail, namely NaCl and KCl, for the two previously mentioned repulsive interaction forms. The separation between the symmetric and antisymmetric state was .29eV for KCl for both forms of the repulsive interaction. This may be compared to a value of .46eV which was found experimentally by Gramm[11] for the F_A-centre. Our saddle-point defect differs from that considered by Gramm in that he has one of the group 1 ions replaced by an impurity cation. However one would still expect order of magnitude agreement in the separation between the symmetric and antisymmetric states which is the case.

FIGURE 8.

Energy level diagram for NaCl for a Born-Mayer nearest neighbour repulsive interaction. E_{AB} and E_{EM} are the F-centre absorption and emission energies respectively and E_{AC} is the activation energy for F-centre step diffusion. E_G, E'_G, E_{EX} and E'_{EX} are the relaxed and unrelaxed F-centre ground and excited state energies respectively. E_A and E_S are the antisymmetric and symmetric saddle-point energies from the first calculation while E'_A and E'_S are these energies corrected by replacing $V_L^{FC}(\underline{0})-V_L^{V}(\underline{0})$ by the experimental activation energy for vacancy diffusion.

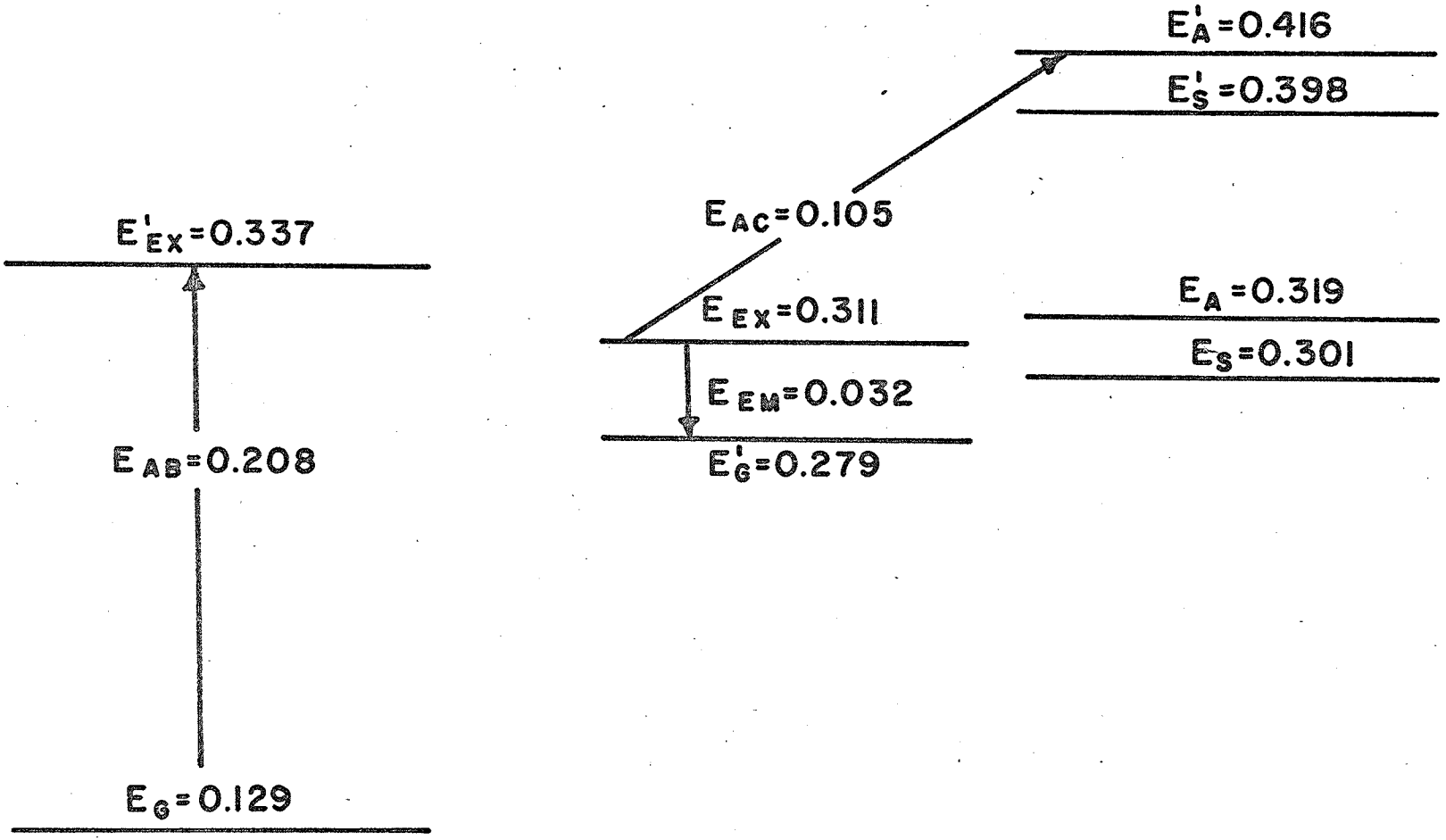

$E'_{EX}=0.337$
$E_{AB}=0.208$
$E_G=0.129$
$E'_A=0.416$
$E'_S=0.398$
$E_{AC}=0.105$
$E_{EX}=0.311$
$E_{EM}=0.032$
$E'_G=0.279$
$E_A=0.319$
$E_S=0.301$

FIGURE 9.

Energy level diagram for NaCl for an inverse power nearest neighbour repulsive interaction. The explanation of the various energies is given in the caption for figure 8.

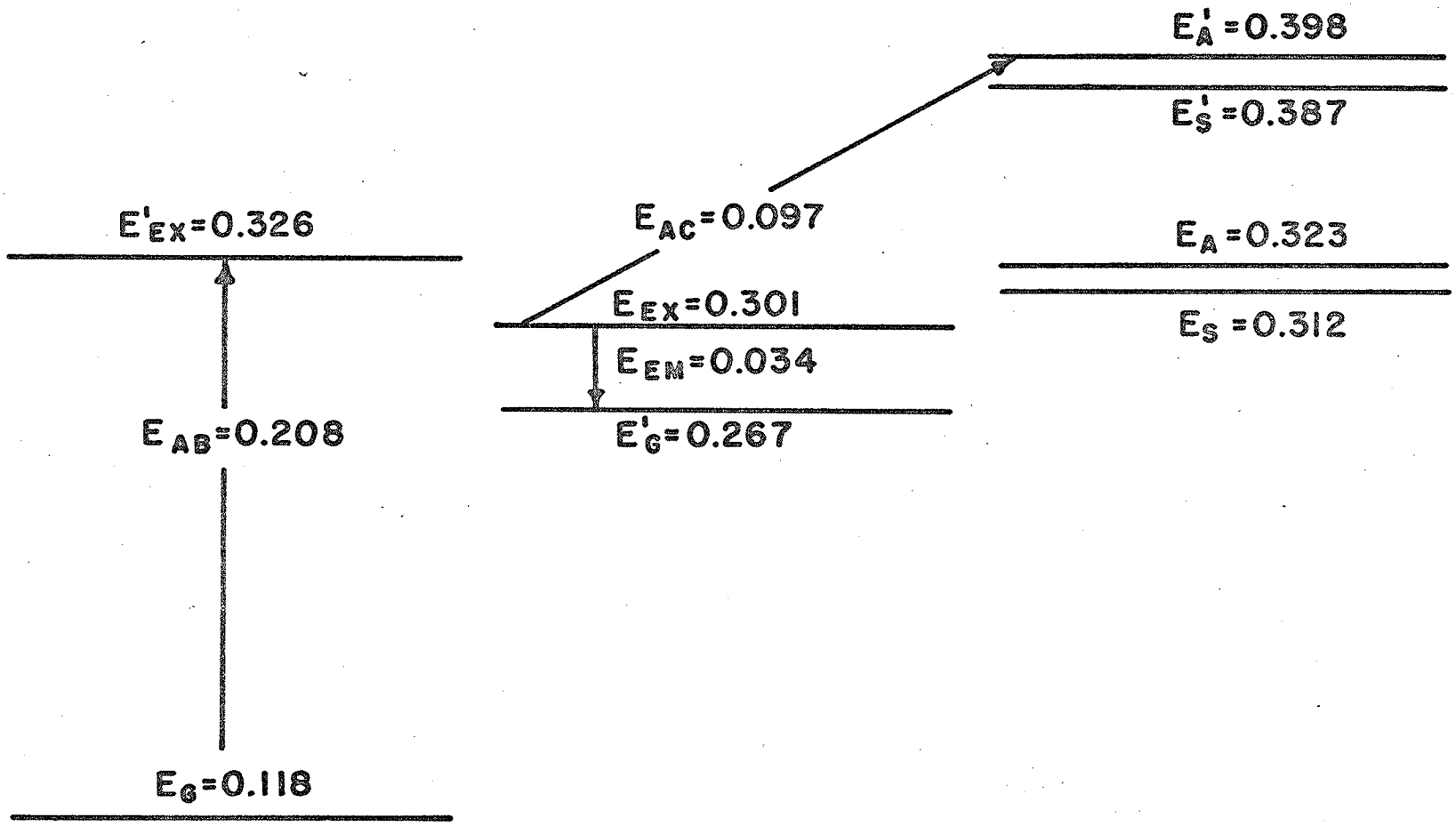

$E'_A = 0.398$
$E'_S = 0.387$
$E_{AC} = 0.097$
$E'_{EX} = 0.326$
$E_A = 0.323$
$E_{EX} = 0.301$
$E_S = 0.312$
$E_{EM} = 0.034$
$E_{AB} = 0.208$
$E'_G = 0.267$
$E_G = 0.118$

FIGURE 10.

Energy level diagram for KCl for a Born-Mayer nearest neighbour repulsive interaction. The explanation of the various energies is given in the caption for figure 9.

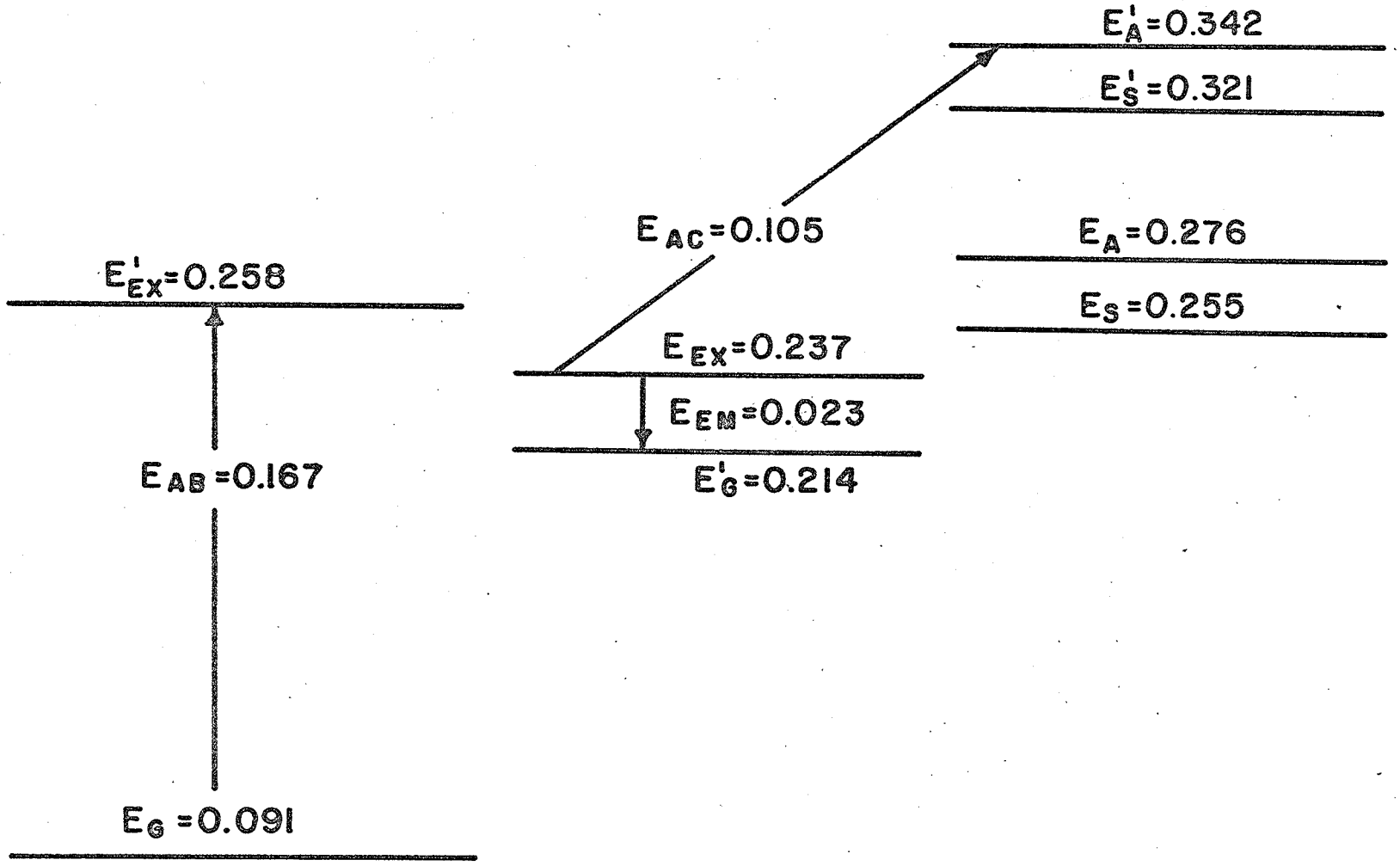
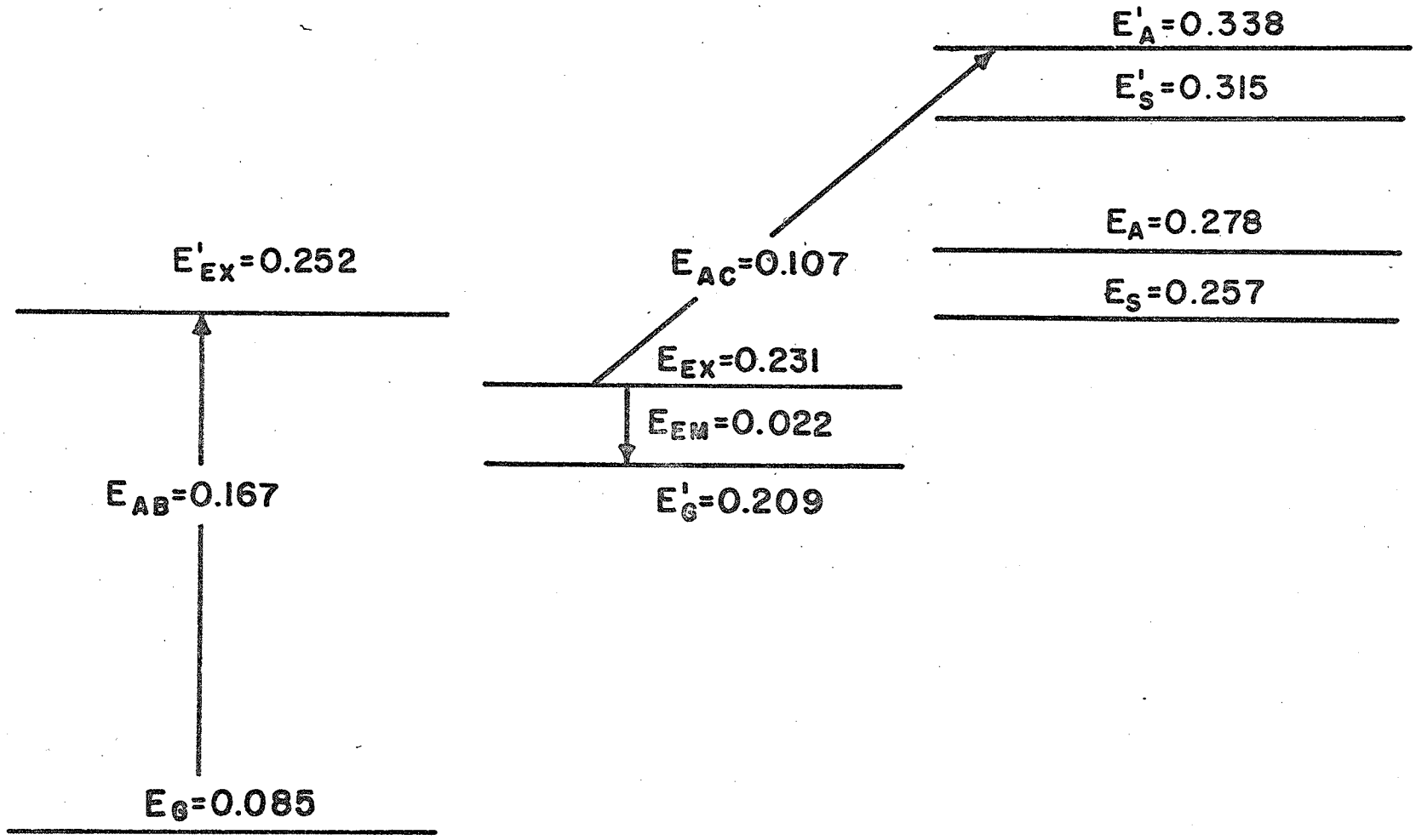

$E'_A = 0.342$
$E'_S = 0.321$
$E_{AC} = 0.105$
$E_A = 0.276$
$E_S = 0.255$
$E'_{EX} = 0.258$
$E_{EX} = 0.237$
$E_{EM} = 0.023$
$E_{AB} = 0.167$
$E'_G = 0.214$
$E_G = 0.091$

FIGURE 11.

Energy level diagram for KCl for an inverse power nearest neighbour repulsive interaction. The explanation of the various energies is given in the caption for figure 8.


E'A=0.338
E's=0.315
EA=0.278
ES=0.257
E'EX=0.252
EAC=0.107
EEX=0.231
EEM=0.022
EAB=0.167
E'G=0.209
EG=0.085

The activation energy for F-centre step diffusion (difference in energy between the relaxed antisymmetric saddle-point state and the relaxed F-centre excited state) does not agree well with the value quoted by Wolf[1] of 1.6±.2eV for KCl. It has been determined[32] that reorientation of an F_A-centre occurs from the excited F_A-centre state. Since an F_A-centre is just an F-centre with an impurity cation at one of the nearest neighbour sites and reorientation corresponds to our step diffusion process it has been assumed that the step diffusion process also originates from the excited F-centre state. It was felt that since the repulsive parameters of the overlap potential are in doubt (the repulsive energy is evaluated at distances which differ greatly from the bulk equilibrium nearest neighbour distance) it may be better to replace $V_L^{S.P.}(\underline{o}) - V_L^{V}(\underline{o})$ where $V_L^{S.P.}(\underline{o})$ is the change in energy of a perfect undistorted lattice by the introduction of a saddle-point defect and $V_L^{V}(\underline{o})$ is the change in energy of a perfect undistorted lattice by the introduction of an anion vacancy, by the experimental value for vacancy diffusion. This quantity $V_L^{S.P.}(\underline{o}) - V_L^{V}(\underline{o})$ is not the actual theoretical activation energy but only an approximation because the distortion field must be taken into account. That is the lattice is continuously relaxing, as the anion moves from its perfect lattice position to a neighbouring vacancy through the saddle-point configuration, so as to keep the crystal in its lowest

energy configuration. The experimental values for the activation energies for vacancy diffusion are given by R. G. Fuller[35] for KCl and N. Laurance[36] for NaCl. The resulting corrected values for the energy levels of the saddle-point configuration are given in tables 10 and 11 and figures 8-11.

It can be seen that this correction raises the energy levels of the symmetric and antisymmetric states of the saddle-point considerably. The energy difference between the relaxed F-centre excited state and the antisymmetric state now agrees quite closely with experiment. These are respectively 1.42eV and 1.45eV for the Born-Mayer and inverse power forms of the repulsive interaction compared to a value of $1.6 \pm .2$eV quoted by Wolf.[1] This correction to the saddle-point energy levels did not however change the separation between the symmetric and antisymmetric states which remained .29eV.

As before polarization effects were not considered in this calculation. The inclusion of polarization would probably require a three-parameter minimization in the zeroth order calculation as one would likely have to regard the dipole moment on the group 1 ions as one component of the $\underline{\lambda}$ rather than a component of the $\underline{\xi}$.

TABLE 10. CORRECTED SADDLE POINT ENERGIES (NaCl)

symmetry	antisymmetric		symmetric	
type of repulsive interaction	Born-Mayer	inverse power	Born-Mayer	inverse power
$V_L^{S.P.}(\underline{0})$	.573	.573	.573	.573
$V_L^{V}(\underline{0})$	.582	.570	.581	.570
$V_L^{S.P.}(\underline{0}) - V_L^{V}(\underline{0})$	-.018	.003	-.019	.003
activation energy for vacancy diffusion	.078*	.078*	.078*	.078*
$E(\underline{\xi},\underline{\lambda}) - U_0$	.319	.323	.301	.312
corrected $E(\underline{\xi},\underline{\lambda}) - U_0$	.416	.398	.398	.387

All energies are in rydbergs.

* values from reference 36.

TABLE 11. CORRECTED SADDLE-POINT ENERGIES (KCl)

symmetry	antisymmetric		symmetric	
type of repulsive interaction	Born-Mayer	inverse power	Born-Mayer	inverse power
$V_L^{S.P.}(\underline{o})$	.532	.532	.532	.532
$V_L^{v}(\underline{o})$	.527	.522	.527	.521
$V_L^{S.P.}(\underline{o}) - V_L^{v}(\underline{o})$	.004	.010	.004	.010
activation energy for vacancy diffusion	.070*	.070*	.070*	.070*
$E(\underline{\xi}, \underline{\lambda}) - U_o$	.276	.278	.255	.255
corrected $E(\underline{\xi}, \underline{\lambda}) - U_o$	.342	.338	.321	.315

All energies are in rydbergs.

* values from reference 35 (uncertainty in value is .007)

CHAPTER IV

SUMMARY

Using a gaussian for the F-centre ground state pseudo wave function it was found that the F-centre electron was well localized within the anion vacancy and lattice relaxation, ignoring ionic polarization, was small. The F-centre excited state pseudo wave function was likewise compact, peaking at a distance of about .6a from the centre of the defect (a = equilibrium interionic spacing). These excited state functions were very similar to those found by Gourary and Adrian[26] but differed substantially from that found by W. Beall Fowler.[28]

The calculated absorption energies for the ordinary F-centre agreed well with experiment, based on semi-empirical pseudopotential ion size parameters derived from the absorption energy with Gourary-Adrian wave functions. This does show that a gaussian pseudo wave function is a valid form to use in an F-centre ground state energy calculation. My calculated values for the absorption energy were 2.83eV and 2.28eV for NaCl and KCl respectively compared to the experimental values of 2.77eV and 2.30eV.[4] My calculated emission energies were lower than the experimental values, being .46eV and .31eV for NaCl and KCl respectively compared to the experimental values of .98eV and 1.21eV.[4]

The ion size contribution to the interaction between the F-centre electron and the crystal was positive in all cases

(compared to a negative value for the interaction energy considering the ions as point charges) and ranged from .6% to 3.8% of the point ion contribution for the ground state and from 3.1% to 8.8% for the excited state. Hence this ion size effect is non-negligible.

It is felt that relaxation of the Franck-Condon principle and the inclusion of electronic polarization may improve the agreement between my emission energies and experiment. To my knowledge there has been no fully satisfactory theoretical treatment of the emission process.

For the saddle-point configuration the system may exist in either a symmetric or an antisymmetric state, where the excess electron is described by pseudo wave functions $\Phi_S = A_3 z e^{-\alpha^2 r^2}$ and $\Phi_A = A_3 e^{-\alpha^2 r^2}$ respectively (the symmetric state is lower in energy). Φ_A was found to peak at r = .7a from the migrating anion while Φ_S peaked at about r = a. The distortion fields associated with the relaxation of these two states were qualitatively the same but a little larger for the antisymmetric state, resulting in a larger change in energy upon relaxation of the energy of the state. As before, ion size effects were non-negligible, ranging from 3.9% to 13.6% of the point ion contribution.

This calculation was initially carried out for a Born-Mayer nearest neighbour repulsive interaction, but it was felt that this form may break down when the ions are pushed too close together, as could be the case at the saddle-point,

so an inverse power form for this interaction was also used. The results using the two different forms were very similar.

The separation between symmetric and antisymmetric states was .29eV compared to an experimental value of .46eV[11] for F_A emission. However the physical picture for F_A emission is slightly different from that considered in my calculation in that one of the nearest neighbour cations to the migrating anion is an impurity ion, and also, the final state would be unrelaxed.

The activation energy for F-centre step diffusion is assumed to correspond to the difference in energy between the relaxed antisymmetric state of the saddle-point and the relaxed F-centre excited state.[32] My value for this energy difference did not agree with experiment until a correction was made to the zeroth order energy of the system. This correction was motivated by the fact that the parameters of the nearest neighbour repulsive interaction were calculated for ions having the bulk equilibrium lattice spacing, while near the migrating anion the separation of ions may differ substantially from this value. That is $V_L^{S.P.}(\underline{o}) - V_L^{V}(\underline{o})$ where $V_L^{S.P.}(\underline{o})$ is the change in energy of an undistorted lattice by the introduction of a saddle-point defect and $V_L^{V}(\underline{o})$ is the change in energy of an undistorted lattice by the introduction of an anion vacancy, is replaced by the experimental value for the vacancy diffusion activation energy. (This theoretical expression is only an approximation

because one has not taken proper account of the changing lattice relaxation). When this correction was applied, the calculated activation energies for F-centre step diffusion became 1.42eV and 1.45eV for KCl for the Born-Mayer and inverse power forms of the repulsive interaction respectively, compared to an experimental value of 1.6±.2eV. This correction did not change the separation between the symmetric and antisymmetric states. Also, polarization was not taken into account in this saddle-point calculation.

The disagreement with experiment of my emission energies for the ordinary F-centre emphasize the need to investigate the effect that ionic polarization has on the energy states and to review the various assumptions involved such as the adiabatic approximation and the Franck-Condon principle.

The results of the saddle-point calculations point out the need to redetermine the nearest neighbour repulsive ion-ion interaction parameters when defect configurations are examined which do not involve small perturbations of the perfect lattice structure. However the results do indicate that correcting for this repulsive interaction a good description of the saddle-point configuration results which may be adapted to other studies such as F_A, F_B, and F_C defect centres.

REFERENCES

1. E. L. Wolf, Phys. Rev. 142, 555 (1966).
2. F. Lüty, in Physics of Colour Centres, edited by W. Beall Fowler, Academic Press Inc., New York, 1968, chapter 3.
3. I. Schneider, Phys. Rev. 177, 1324 (1969).
4. W. Gerbhardt and H. Kuhnert, Phys. Letters 11, 15 (1964).
5. B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. 127, 276 (1962).
6. M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).
7. J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).
8. H. Kanzaki, J. Phys. Chem. Solids 2, 24 (1957).
9. R. H. Bartram, A. M. Stoneham, and P. Gash, Phys. Rev. 176, 1014 (1968).
10. A. M. Stoneham, International Symposium on Colour Centres in Alkali Halides, Rome, 1968, abstract no. 182.
11. G. Gramm, Phys. Letters 8, 157 (1964)
12. N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).
13. H. Kanzaki, J. Phys. Chem. Solids 2, 107 (1957).
14. E. W. Kellerman, Phil. Trans. Roy. Soc. 23B, 513 (1940).
15. A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. 119, 980 (1960).
16. F. Herman, J. Phys. Chem. Solids 8, 405 (1959).
17. R. H. Lyddane and K. F. Herzfeld, Phys. Rev. 54, 846 (1938).

18. B. Szigeti, Trans. Faraday Soc. 45, 155 (1949).

19. M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, 1954, pp 82-116.

20. B. G. Dick and A. W. Overhauser, Phys. Rev. 112, 90 (1958).

21. W. Cochran, Phys. Rev. Letters 2, 495 (1959).

22. W. Cochran, Proc. Roy. Soc. A253, 260 (1959).

23. W. Cochran, Phil. Mag. 4, 1082 (1959).

24. E. E. Havinga, Phys. Rev. 119, 1193 (1960).

25. R. A. Cowley, Proc. Roy. Soc. A268, 121 (1962).

26. B. S. Gourary and F. J. Adrian, Phys. Rev. 105, 1180 (1957).

27. R. F. Wood and H. W. Joy, Phys. Rev. 136, A451 (1964).

28. W. Beall Fowler, Phys. Rev. 135, A1745 (1964).

29. U. Öpik and R. F. Wood, Phys. Rev. 179, 772 (1969).

30. U. Öpik and R. F. Wood, Phys. Rev. 179, 783 (1969).

31. B. Dayal and B. B. Tripathi, Proc. Phys. Soc. 77, 303 (1961).

32. F. Lüty, in Physics of Colour Centres, edited by W. Beall Fowler, Academic Press Inc., New York, 1968, p. 212.

33. M. J. D. Powell, Computer Journal 7, 303 (1965).

34. M. P. Tosi, in Solid State Physics Volume 16, edited by F. Seitz and D. Turnbull, Academic Press Inc., New York, 1964, p. 6.

35. R. G. Fuller, Phys. Rev. 142, 524 (1966).

36. N. Laurance, Phys. Rev. 120, 57 (1960).

37. P. M. Morse and H. Feshbach, Methods of Theoretical Physics Part II, McGraw-Hill Book Co. Inc., New York, 1953, p. 1274.

APPENDIX A

EXPECTATION VALUE OF $\langle \Phi | V_{PI} | \Phi \rangle$

The potential energy of an electron in the presence of an assembly of point charges may be written as

$$V_{PI}(\vec{r}) = -2 \sum_i \frac{Q_i}{|\vec{r} - \vec{r}_i|}$$

where energy is expressed in rydbergs (hence the factor 2), charge Q_i is in units of $|e|$ and length is in units of the first Bohr orbit a_0 where $a_0 = \dfrac{\hbar^2}{m_e e^2} = 5.29172 \times 10^{-9}$ cm.

and m_e is the electronic mass.

This may be rewritten as

$$V_{PI}(\vec{r}) = -2 \sum_i Q_i \sum_{\ell=0}^{\infty} \frac{1}{r_>} \left[\frac{r_<}{r_>} \right]^{\ell} P_\ell^0(\cos\gamma_i)$$

where $r_{\gtrless}$ is the $\left\{ \begin{matrix} \text{larger} \\ \text{smaller} \end{matrix} \right\}$ of $|\vec{r}|$ and $|\vec{r}_i|$

and $P_\ell^0(\cos\gamma_i)$ are spherical harmonics where γ_i is the angle between $\vec{r}$ and $\vec{r}_i$.

$$\therefore V_{PI}(\vec{r}) = -2 \sum_{\substack{i \\ (r_i < r) \\ (r_i \neq 0)}} \sum_{\ell=0}^{\infty} Q_i \left(\frac{r_i^{\ell}}{r^{\ell+1}} \right) P_\ell^0(\cos\gamma_i) - \frac{2Q_0}{r}$$

$$- 2 \sum_{\substack{i \\ (r \leq r_i) \\ (r_i \neq 0)}} \sum_{\ell=0}^{\infty} Q_i \left(\frac{r^{\ell}}{r_i^{\ell+1}} \right) P_\ell^0(\cos\gamma_i) \qquad \text{(A1)}$$

where Q_0 is the charge on the ion at $\vec{r}_i = \vec{0}$.

In order to put this second term into a form which is easier to handle consider adding to and subtracting from equation (A1) the term $2 \sum_{\substack{i \\ (r_i < r) \\ (r_i \neq 0)}} \sum_{l=0}^{\infty} Q_i \left(\frac{r^l}{r_i^{l+1}} \right) P_l^0(\cos\gamma_i)$

$$\therefore V_{PI}(\vec{r}) = -2 \sum_{\substack{i \\ (r_i \neq 0)}} Q_i \sum_{l=0}^{\infty} \left(\frac{r^l}{r_i^{l+1}} \right) P_l^0(\cos\gamma_i)$$

$$+ 2 \sum_{\substack{i \\ (r_i < r) \\ (r_i \neq 0)}} Q_i \sum_{l=0}^{\infty} \left[\frac{r^l}{r_i^{l+1}} - \frac{r_i^l}{r^{l+1}} \right] P_l^0(\cos\gamma_i) \qquad (A2)$$

$$- \frac{2Q_0}{r}$$

It is now necessary to find the relationship between γ_i and the spherical polar angle Θ which is used in this problem. From reference 37

$$P_l^m(\cos\gamma_i) = \sum_{m=0}^{l} \epsilon_m \frac{(l-m)!}{(l+m)!} P_l^m(\cos\Theta_i) P_l^m(\cos\Theta) \cos\left[m(\phi - \phi_i)\right]$$

where $\epsilon_0 = 1$

$\epsilon_m = 2$ for $m = 2, 3, 4, \ldots\ldots$

Thus substituting into equation (A2) one obtains

$$V_{PI}(\vec{r}) = -2 \sum_{\substack{i \\ (r_i \neq 0)}} \sum_{l=0}^{\infty} \sum_{m=0}^{l} \left\{ Q_i \left(\frac{r^l}{r_i^{l+1}} \right) \epsilon_m \frac{(l-m)!}{(l+m)!} P_l^m(\cos\Theta_i) \right.$$

$$\left. P_l^m(\cos\Theta) \cos\left[m(\phi - \phi_i)\right] \right\} - \frac{2Q_0}{r}$$

$$+2\sum_{\substack{i\\(r_i<r)\\(r_i\neq 0)}}\sum_{l=0}^{\infty}\sum_{m=0}^{l}\left\{Q_i\left[\frac{r^l}{r_i^{l+1}}-\frac{r_i^l}{r^{l+1}}\right]\epsilon_m\frac{(l-m)!}{(l+m)!}P_l^m(\cos\Theta_i)\right.$$

$$\left.P_l^m(\cos\Theta)\cos\left[m(\phi-\phi_i)\right]\right\} \qquad (A3)$$

It is possible to simplify this expression considerably in the calculation of $\langle\Phi|V_{PI}|\Phi\rangle$ due to the orthogonality of the spherical harmonics, provided Φ is a simple linear combination of spherical harmonics.

A. F-CENTRE GROUND STATE

In this spherically symmetric case the pseudo wave function Φ was chosen to contain only an $l = 0$ term. Hence only the terms from equation (A3) corresponding to $l = 0$ contribute to $\langle\Phi|V_{PI}|\Phi\rangle$. Hence, we may use an effective $V_{PI}(\vec{r})$ given by

$$V_{PI}(\vec{r})=-2\sum_{\substack{i\\(r_i\neq 0)}}\left(\frac{Q_i}{r_i}\right)+2\sum_{\substack{i\\(r_i<r)\\(r_i\neq 0)}}Q_i\left[\frac{1}{r_i}-\frac{1}{r}\right] \qquad (A4)$$

since $Q_o = 0$ for an ordinary F-centre.

Thus

$$\langle\Phi|V_{PI}|\Phi\rangle = -2\sum_{\substack{i\\(r_i\neq 0)}}\left(\frac{Q_i}{r_i}\right)$$

$$+2\sum_{\substack{i\\(r_i\neq 0)}}\int_{r_i}^{\infty}|\Phi|^2 Q_i\left[\frac{1}{r_i}-\frac{1}{r}\right]d\tau \qquad (A5)$$

B. F-CENTRE EXCITED STATE

The wave function for the F-centre excited state has $\ell = 1$ dependence and hence the $\ell = 0$ and $\ell = 2$ terms of $V_{PI}(\vec{r})$ given by equation (A3) contribute to $\langle\Phi|V_{PI}|\Phi\rangle$ since $|\Phi|^2$ may be written as a linear combination of $\ell = 0$ and $\ell = 2$ terms. Furthermore the terms in $V_{PI}(\vec{r})$ for $m > 0$ do not contribute to $\langle\Phi|V_{PI}|\Phi\rangle$ if Φ is assumed to have no dependence on the azimuthal angle ϕ. Hence from equation (A3)

$$V_{PI}(\vec{r}) = -2\sum_{\substack{i \\ (r_i \neq 0)}}\left(\frac{Q_i}{r_i}\right) - 2\sum_{\substack{i \\ (r_i \neq 0)}} Q_i\left(\frac{r^2}{r_i^3}\right) P_2^0(\cos\theta)\, P_2^0(\cos\theta_i)$$

$$+ 2\sum_{\substack{i \\ (r_i \neq 0) \\ (r_i < r)}} Q_i\left[\frac{1}{r_i} - \frac{1}{r}\right]$$

$$+ 2\sum_{\substack{i \\ (r_i \neq 0) \\ (r_i < r)}} Q_i\left[\frac{r^2}{r_i^3} - \frac{r_i^2}{r^3}\right] P_{\frac{4}{2}}^0(\cos\theta_i)\, P_{\frac{4}{2}}^0(\cos\theta) \qquad \text{(A6)}$$

where again Q_0 is zero for the F-centre.

C. SADDLE-POINT CASE

1. ANTI-SYMMETRIC STATE

The pseudo wave function Φ_A is assumed to have $\ell = 1$ dependence. Hence the expression for $V_{PI}(\vec{r})$ is the same as equation (A6) only one more term, namely $\left(-\frac{2Q_0}{r}\right)$ is added which takes account of the contribution to the potential of the ion at the origin. Note however, that a different co-ordinate system is used for the saddle-point case, hence

different values of r_i and θ_i will be used from those in equation (A6) for the ordinary F-centre. Thus

$$V_{PI}(\vec{r}) = -2 \sum_{\substack{i \\ (r_i \neq 0)}} \left(\frac{Q_i}{r_i}\right) - 2 \sum_{\substack{i \\ (r_i \neq 0)}} Q_i \left(\frac{r^2}{r_i^3}\right) P_2^0(\cos\theta) P_2^0(\cos\theta_i)$$

$$+2 \sum_{\substack{i \\ (r_i < r) \\ (r_i \neq 0)}} Q_i \left[\frac{1}{r_i} - \frac{1}{r}\right] - \frac{2Q_0}{r}$$

$$+2 \sum_{\substack{i \\ (r_i < r) \\ (r_i \neq 0)}} Q_i \left[\frac{r^2}{r_i^3} - \frac{r_i^2}{r^3}\right] P_2^0(\cos\theta) P_2^0(\cos\theta_i) \qquad \text{(A7)}$$

2. SYMMETRIC CASE

In this case Φ_s has $\ell = 0$ and $\ell = 2$ dependence hence may be written as a linear combination of $\ell = 0$, 2, and 4 terms, hence $V_{PI}(\vec{r})$ must include the $\ell = 0$, 2 and 4 contributions. Thus for the symmetric saddle-point state the effective $V_{PI}(\vec{r})$ which must be used to calculate $\langle\Phi|V_{PI}|\Phi\rangle$ is

$$V_{PI}(\vec{r}) = -2 \sum_{\substack{i \\ (r_i \neq 0)}} \left[Q_i \left\{ \frac{1}{r_i} + \frac{r^2}{r_i^3} P_2^0(\cos\theta) P_2^0(\cos\theta_i) \right.\right.$$

$$\left.\left. + \frac{r^4}{r_i^5} P_4^0(\cos\theta) P_4^0(\cos\theta_i) \right\}\right] - \frac{2Q_0}{r}$$

$$+ 2 \sum_{\substack{i \\ (r_i < r) \\ (r_i \neq 0)}} \left[Q_i \left\{ \left(\frac{1}{r_i} - \frac{1}{r} \right) + \left(\frac{r^2}{r_i^3} - \frac{r_i^2}{r^3} \right) P_2^0(\cos\Theta) P_2^0(\cos\Theta_i) \right.\right.$$

$$\left.\left. + \left(\frac{r^4}{r_i^5} - \frac{r_i^4}{r^5} \right) P_4^0(\cos\Theta) P_4^0(\cos\Theta_i) \right\} \right] \qquad \text{(A8)}$$

APPENDIX B

GROUPING OF IONS IN CALCULATION OF DISTORTION COEFFICIENTS AND DISPLACEMENTS

In order to facilitate the calculation for the distortion coefficients one can group the ions which make equal contributions to the sum in equation (36) and hence reduce the number of terms which arise in the expansion. That is

$$G_\alpha(\vec{q}) = \frac{1}{N} \sum_i' \sum_{l_i}' F_\alpha(\vec{r}_K^{\,l_i})\, e^{i\vec{q}\cdot\vec{r}_K^{\,l_i}} \qquad (B1)$$

where the sum over i is now a sum over groups. In practice one casts this equation into a simplier form by noting that $F_\alpha(\vec{r}_K^{\,l}) = -F_\alpha(-\vec{r}_K^{\,l})$ since there is inversion symmetry through the origin for all the defects considered in this work. Hence

$$G_\alpha(\vec{q}) = \frac{2i}{N} \sum_i' \sum_{l_i}' F_\alpha(\vec{r}_K^{\,l_i}) \sin(\vec{q}\cdot\vec{r}_K^{\,l_i}) \qquad (B2)$$

where the sum over l_i is now only over inversion pairs (that is in considering the contribution from the ion at say (x,y,z) one also includes the contribution from the ion at (-x,-y,-z)).

A. F-CENTRE GROUND STATE

For this spherically symmetrical case the summation over i ranges from one to four where one denotes the nearest neighbour contribution, two the second nearest neighbour and so on. The explicit expressions for $\underline{G}(\vec{q})$ are given below. $\underline{G}(\vec{q})$ is a six component column vector where the first three components refer to x, y, z components of the cations and the next three components refer to the x, y, z components of the

anions. The nearest neighbour contribution to $\underline{G}(\vec{q})$ is

$$\underline{G}(\vec{q})_{I} = \frac{2i F_x(100)}{N} \begin{pmatrix} \sin g_x a \\ \sin g_y a \\ \sin g_z a \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \text{(B3)}$$

where $F_X(100)$ is defined following equation (31) where $\vec{r}_K^{\,\ell} = \vec{r}(100)$. The contribution from second nearest neighbours is

$$\underline{G}(\vec{q})_{II} = \frac{2i F_x(110)}{N} \begin{pmatrix} 0 \\ 0 \\ 0 \\ \sin(g_x a)(\cos g_y a + \cos g_z a) \\ \sin(g_y a)(\cos g_x a + \cos g_z a) \\ \sin(g_z a)(\cos g_x a + \cos g_y a) \end{pmatrix} \qquad \text{(B4)}$$

Similarly the contribution due to third and fourth nearest neighbours are

$$\underline{G}(\vec{q})_{III} = \frac{2i F_x(1,1,1)}{N} \begin{pmatrix} \sin(g_x a + g_y a + g_z a) + \sin(g_x a - g_y a + g_z a) \\ \quad + \sin(g_x a + g_y a - g_z a) + \sin(g_x a - g_y a - g_z a) \\ \sin(g_x a + g_y a + g_z a) - \sin(g_x a - g_y a + g_z a) \\ \quad + \sin(g_x a + g_y a - g_z a) - \sin(g_x a - g_y a - g_z a) \\ \sin(g_x a + g_y a + g_z a) + \sin(g_x a - g_y a + g_z a) \\ \quad - \sin(g_x a + g_y a - g_z a) - \sin(g_x a - g_y a - g_z a) \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \text{(B5)}$$

and

$$\underline{G}(\vec{q})_{\underline{IV}} = \frac{2i F_x(200)}{N} \begin{pmatrix} 0 \\ 0 \\ 0 \\ \sin(2q_x a) \\ \sin(2q_y a) \\ \sin(2q_z a) \end{pmatrix} \qquad (B6)$$

B. F-CENTRE EXCITED STATE

When the F-centre electron is in an excited state described by a pseudo wave function of the form $\Phi_{n\ell} = A_n \cos\theta\, \ell^{-\alpha^2 r^2}$ there is symmetry about the polar axis. Now it is not possible to group the ions simply according to their distance from the defect for one must also account for the fact that there is no longer the same inversion symmetry through all three co-ordinate planes. In calculating the distortions for the F-centre excited state the sum in equation (36) was split into seven groups as follows (the full group will include also the ions arrived at by inversion of these through the origin).

group 1	(1,0,0), (0,1,0)
group 2	(0,0,1)
group 3	(1,1,0), (1,$\bar{1}$,0)
group 4	(1,0,1), (0,1,1), (1,0,$\bar{1}$), (0,1,$\bar{1}$)
group 5	(1,1,1), (1,$\bar{1}$,1), (1,1,$\bar{1}$), (1,$\bar{1}$,$\bar{1}$)
group 6	(2,0,0), (0,2,0)
group 7	(0,0,2)

Actually the extent of the sum in equation (B2) which was considered (that is the number of ions considered) for the spherically symmetric and this case was the same, only due to less symmetry in this latter case the number of terms in the calculation is greater. The explicit expressions for $\underline{G}(\vec{q})$ due to these different groups are

$$\underline{G}(\vec{q})_{I} = \frac{2i F_x(100)}{N} \begin{pmatrix} \sin g_x a \\ \sin g_y a \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{B7}$$

$$\underline{G}(\vec{q})_{II} = \frac{2i F_z(001)}{N} \begin{pmatrix} 0 \\ 0 \\ \sin g_z a \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{B8}$$

$$\underline{G}(\vec{q})_{III} = \frac{2i F_x(110)}{N} \begin{pmatrix} 0 \\ 0 \\ 0 \\ \sin(g_x a + g_y a) + \sin(g_x a - g_y a) \\ \sin(g_x a + g_y a) - \sin(g_x a - g_y a) \\ 0 \end{pmatrix} \tag{B9}$$

$$\underline{G}\left(\vec{q}_0\right)_{\underline{IV}} = \frac{2i}{N}\begin{pmatrix} 0 \\ 0 \\ 0 \\ F_x(101)\left[\sin(q_x a + q_3 a) + \sin(q_x a - q_3 a)\right] \\ F_x(101)\left[\sin(q_y a + q_3 a) - \sin(-q_y a + q_3 a)\right] \\ F_z(101)\left[\sin(q_y a + q_3 a) + \sin(-q_y a + q_3 a) \right. \\ \qquad \left. + \sin(q_x a + q_3 a) \mp \sin(q_x a - q_3 a)\right] \end{pmatrix} \tag{B10}$$

$$\underline{G}\left(\vec{q}_0\right)_{\underline{V}} = \frac{2i}{N}\begin{pmatrix} F_x(111)\left[\sin(q_x a + q_y a + q_3 a) + \sin(q_x a - q_y a + q_3 a) \right. \\ \qquad \left. + \sin(q_x a + q_y a - q_3 a) + \sin(q_x a - q_y a - q_3 a)\right] \\ F_x(111)\left[\sin(q_x a + q_y a + q_3 a) + \sin(q_x a + q_y a - q_3 a) \right. \\ \qquad \left. - \sin(q_x a - q_y a - q_3 a) - \sin(q_x a - q_y a + q_3 a)\right] \\ F_3(111)\left[\sin(q_x a + q_y a + q_3 a) + \sin(q_x a - q_y a + q_3 a) \right. \\ \qquad \left. - \sin(q_x a + q_y a - q_3 a) - \sin(q_x a - q_y a - q_3 a)\right] \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{B11}$$

$$\underline{G}\left(\vec{q}_0\right)_{\underline{VI}} = \frac{2i}{N} F_x(200)\begin{pmatrix} 0 \\ 0 \\ 0 \\ \sin(2q_x a) \\ \sin(2q_y a) \\ 0 \end{pmatrix} \tag{B12}$$

$$\underline{G}\left(\vec{q}_0\right)_{\underline{VII}} = \frac{2i\,F_z(002)}{N}\begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \sin(2q_3 a) \end{pmatrix} \tag{B13}$$

In the actual calculation one can save machine time by computing the contributions from various groups at the same time. For instance I calculated the contributions from groups I and IV, groups II and III, and groups V, VI and VII at the same time. This is possible because upon adding the $\underline{G}(\vec{q}_\delta)$ for these groups one doesn't add two finite components together. That is where one $\underline{G}(\vec{q}_\delta)_i$ has a finite component the others added to it have zeros. However one must be careful when using such an approach that the algebraic factors $F_X(200)$, etc. are now brought inside the column vector since in general each component is multiplied by a different factor.

C. SADDLE-POINT CASE

In order to use the $\vec{q}_\delta$ vectors as tabulated by Kellerman[10] it is necessary to do the calculation in the co-ordinate system labelled I in fig. 1. Then one transforms the result back to co-ordinate system II so as to express the displacement in the defect orientated co-ordinate system. As an illustration of the transformations involved consider the contribution to $\underline{G}(\vec{q}_\delta)$ from the ions in group 2. This group consists of cations at (1, 1/2, 1/2) and (1,-1/2,-1/2) and anions at (1,1/2,-1/2) and (1,-1/2,1/2) plus the ions arrived at by inversion through the origin. Hence $\underline{G}(\vec{q}_\delta)_{\overline{II}}$ due to this group is

$$\underline{G}(\vec{q})_{\alpha\beta}^{II} = \frac{2i}{N}\begin{pmatrix} F_x^I(1,\frac{1}{2},\frac{1}{2})\sin(q_x a)\left[\cos\left(\frac{q_y a}{2}\right)\cos\left(\frac{q_3 a}{2}\right) - \sin\left(\frac{q_y a}{2}\right)\sin\left(\frac{q_3 a}{2}\right)\right] \\ F_Y^I(1,\frac{1}{2},\frac{1}{2})\cos(q_x a)\left[\sin\left(\frac{q_y a}{2}\right)\cos\left(\frac{q_3 a}{2}\right) + \cos\left(q_y \frac{a}{2}\right)\sin\left(q_3 \frac{a}{2}\right)\right] \\ F_z^I\left(1,\frac{1}{2},\frac{1}{2}\right)\cos(q_x a)\left[\sin\left(q_y \frac{a}{2}\right)\cos\left(q_3 \frac{a}{2}\right) + \cos\left(q_y \frac{a}{2}\right)\sin\left(q_3 \frac{a}{2}\right)\right] \\ F_x^I\left(1,\frac{1}{2},-\frac{1}{2}\right)\sin(q_x a)\left[\cos\left(q_y \frac{a}{2}\right)\cos\left(q_3 \frac{a}{2}\right) + \sin\left(q_y \frac{a}{2}\right)\sin\left(q_3 \frac{a}{2}\right)\right] \\ F_Y^I\left(1,\frac{1}{2},-\frac{1}{2}\right)\cos(q_x a)\left[\sin\left(q_y \frac{a}{2}\right)\cos\left(q_3 \frac{a}{2}\right) - \cos\left(q_y \frac{a}{2}\right)\sin\left(q_3 \frac{a}{2}\right)\right] \\ F_z^I\left(1,\frac{1}{2},-\frac{1}{2}\right)\cos(q_x a)\left[\sin\left(q_y \frac{a}{2}\right)\cos\left(q_3 \frac{a}{2}\right) - \cos\left(q_y \frac{a}{2}\right)\sin\left(q_3 \frac{a}{2}\right)\right] \end{pmatrix} \tag{B14}$$

where $F_x^I(1,1/2,1/2)$ is defined following equation (31) where $\underline{\xi}_\alpha^I$ is the displacement in co-ordinate system I. The relationship between the two co-ordinate systems of fig. 1 is given by

$$\begin{pmatrix} \xi_x^{II} \\ \xi_y^{II} \\ \xi_3^{II} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} \begin{pmatrix} \xi_x^I \\ \xi_y^I \\ \xi_3^I \end{pmatrix} \tag{B15}$$

Hence $$F_x^I = F_x^{II}$$

$$F_y^I = F_y^{II}\frac{\partial \xi_y^{II}}{\partial \xi_y^I} + F_3^{II}\frac{\partial \xi_3^{II}}{\partial \xi_y^I}$$

$$F_y^I = \frac{1}{\sqrt{2}}\left[F_y^{II} + F_3^{II}\right]$$

and $$F_3^I = \frac{1}{\sqrt{2}}\left[F_3^{II} - F_y^{II}\right]$$

One uses this approach because it is easier to calculate the coefficients $F_\alpha(\vec{n}_k^{\,\ell})$ in the defect orientated co-ordinate system.

If one now carries through the calculation to obtain $\underline{Q}_{\ell}(\vec{q})_{\alpha}$ for each $\vec{q}$, α and ion and then fourier transforms again to get back to configuration space, one arrives at an equation of the form

$$\underline{\xi}^{I} = \underline{\underline{T}} \cdot \underline{F}$$

where the components of $\underline{F}$ are given by the factors which are present in the $\underline{G}(\vec{q})_{\alpha}$'s for the different contributions. One now applies the transformation matrix given by equation (B15) to get the displacements of the ions in the defect orientated co-ordinate system.

In this calculation I considered eight groups as contributing to the displacements. This includes all the ions of the crystal which are less than or equal to a distance of approximately 2.5 lattice spacings from the migrating ion at the saddle point. This includes eight nearest neighbours to the migrating ion or 54 ions.

The division of the ions into groups for the saddle-point case was as shown below. It should be noted that one must add to these the ions which are got by inversion through the origin and that the co-ordinates of the ions are given in co-ordinate system II of figure 1.

group 1	$(0,\sqrt{1/2},0)$
group 2	$(1,0,\sqrt{2}/2)$, $(1,0,-\sqrt{2}/2)$, $(1,+\sqrt{2}/2,0)$, $(1,-\sqrt{2}/2,0)$
group 3A	$(0,\sqrt{2}/2,\sqrt{2})$, $(0,\sqrt{2},\sqrt{2}/2)$
group 3B	$(0,\sqrt{2}/2,-\sqrt{2})$, $(0,-\sqrt{2},\sqrt{2}/2)$

group 4A $(1,\sqrt{2},\sqrt{2}/2)$, $(1,-\sqrt{2},-\sqrt{2}/2)$, $(1,\sqrt{2}/2,\sqrt{2})$, $(1,-\sqrt{2}/2,-\sqrt{2})$

group 4B $(1,\sqrt{2},-\sqrt{2}/2)$, $(1,-\sqrt{2},\sqrt{2}/2)$, $(1,-\sqrt{2}/2,\sqrt{2})$, $(1,\sqrt{2}/2,-\sqrt{2})$

group 5 $(0,3\sqrt{2}/2,0)$, $(0,0,3\sqrt{2}/2)$

group 6 $(2,\sqrt{2}/2,0)$, $(2,-\sqrt{2}/2,0)$, $(2,0,\sqrt{2}/2)$, $(2,0,-\sqrt{2}/2)$

group 7 $(1,0,3\sqrt{2}/2)$, $(1,0,-3\sqrt{2}/2)$, $(1,3\sqrt{2}/2,0)$, $(1,-3\sqrt{2}/2,0)$

The expressions for the contributions of these different groups to $\underline{G}(\vec{q})$ are as follows

$$\underline{G}\left(\vec{q}\right)_{\underline{\underline{III\,A}}} = \frac{2i}{N}\begin{pmatrix} 0 \\ F_y^I\left(0,\frac{3}{2},\frac{1}{2}\right)\sin\left(q_y\frac{3a}{2}+q_3\frac{a}{2}\right) \\ F_3^I\left(0,\frac{3}{2},\frac{1}{2}\right)\sin\left(q_y\frac{3a}{2}+q_3\frac{a}{2}\right) \\ 0 \\ F_y^I\left(0,\frac{3}{2},-\frac{1}{2}\right)\sin\left(q_y\frac{3a}{2}-q_3\frac{a}{2}\right) \\ F_3^I\left(0,\frac{3}{2},-\frac{1}{2}\right)\sin\left(q_y\frac{3a}{2}-q_3\frac{a}{2}\right) \end{pmatrix} \tag{B16}$$

$$\underline{G}\left(\vec{q}\right)_{\underline{\underline{III\,B}}} = \frac{2i}{N}\begin{pmatrix} 0 \\ F_y^I\left(0,-\frac{1}{2},-\frac{3}{2}\right)\sin\left(-q_y\frac{a}{2}-q_3\frac{3a}{2}\right) \\ F_3^I\left(0,-\frac{1}{2},-\frac{3}{2}\right)\sin\left(-q_y\frac{a}{2}-q_3\frac{3a}{2}\right) \\ 0 \\ F_y^I\left(0,-\frac{1}{2},\frac{3}{2}\right)\sin\left(-q_y\frac{a}{2}+q_3\frac{3a}{2}\right) \\ F_3^I\left(0,-\frac{1}{2},\frac{3}{2}\right)\sin\left(-q_y\frac{a}{2}+q_3\frac{3a}{2}\right) \end{pmatrix} \tag{B17}$$

$$\underline{\underline{G}}(\vec{q})_{\underline{\underline{IVA}}} = \frac{2i}{N} \begin{pmatrix} F_x^I(1,\frac{3}{2},-\frac{1}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} - q_3 \frac{a}{2}\right) + \sin\left(q_x a - q_y \frac{3a}{2} + q_3 \frac{a}{2}\right)\right] \\ F_y^I(1,\frac{3}{2},-\frac{1}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} - q_3 \frac{a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} + q_3 \frac{a}{2}\right)\right] \\ F_3^I(1,\frac{3}{2},-\frac{1}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} - q_3 \frac{a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} + q_3 \frac{a}{2}\right)\right] \\ F_x^I(1,\frac{3}{2},\frac{1}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} + q_3 \frac{a}{2}\right) + \sin\left(q_x a - q_y \frac{3a}{2} - q_3 \frac{a}{2}\right)\right] \\ F_y^I(1,\frac{3}{2},\frac{1}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} + q_3 \frac{a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} - q_3 \frac{a}{2}\right)\right] \\ F_3^I(1,\frac{3}{2},\frac{1}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} + q_3 \frac{a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} - q_3 \frac{a}{2}\right)\right] \end{pmatrix} \tag{B18}$$

$$\underline{\underline{G}}(\vec{q})_{\underline{\underline{IVB}}} = \frac{2i}{N} \begin{pmatrix} F_x^I(1,\frac{1}{2},-\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{a}{2} - q_3 \frac{3a}{2}\right) + \sin\left(q_x a - q_y \frac{a}{2} + q_3 \frac{3a}{2}\right)\right] \\ F_y^I(1,\frac{1}{2},-\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{a}{2} - q_3 \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{a}{2} + q_3 \frac{3a}{2}\right)\right] \\ F_3^I(1,\frac{1}{2},-\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{a}{2} - q_3 \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{a}{2} + q_3 \frac{3a}{2}\right)\right] \\ F_x^I(1,\frac{1}{2},\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{a}{2} + q_3 \frac{3a}{2}\right) + \sin\left(q_x a - q_y \frac{a}{2} - q_3 \frac{3a}{2}\right)\right] \\ F_y^I(1,\frac{1}{2},\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{a}{2} + q_3 \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{a}{2} - q_3 \frac{3a}{2}\right)\right] \\ F_3^I(1,\frac{1}{2},\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{a}{2} + q_3 \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{a}{2} - q_3 \frac{3a}{2}\right)\right] \end{pmatrix} \tag{B19}$$

$$\underline{G}(\vec{q})_{\underline{V}} = \frac{2i}{N}\begin{pmatrix} 0 \\ F_y^I(0,\frac{3}{2},-\frac{3}{2})\sin\left(q_y\frac{3a}{2} - q_3\frac{3a}{2}\right) \\ F_3^I(0,\frac{3}{2},-\frac{3}{2})\sin\left(q_y\frac{3a}{2} - q_3\frac{3a}{2}\right) \\ 0 \\ F_y^I(0,\frac{3}{2},\frac{3}{2})\sin\left(q_y\frac{3a}{2} + q_3\frac{3a}{2}\right) \\ F_3^I(0,\frac{3}{2},\frac{3}{2})\sin\left(q_y\frac{3a}{2} + q_3\frac{3a}{2}\right) \end{pmatrix} \tag{B20}$$

$$\underline{G}(\vec{q})_{\underline{VI}} = \frac{2i}{N}\begin{pmatrix} F_x^I(2,\frac{1}{2},-\frac{1}{2})\left[\sin\left(2q_x a + q_y\frac{a}{2} - q_3\frac{a}{2}\right) + \sin\left(2q_x a - q_y\frac{a}{2} + q_3\frac{a}{2}\right)\right] \\ F_y^I(2,\frac{1}{2},-\frac{1}{2}\left[\sin\left(2q_x a + q_y\frac{a}{2} - q_3\frac{a}{2}\right) - \sin\left(2q_x a - q_y\frac{a}{2} + q_3\frac{a}{2}\right)\right] \\ F_3^I(2,\frac{1}{2},-\frac{1}{2})\left[\sin\left(2q_x a + q_y\frac{a}{2} - q_3\frac{a}{2}\right) - \sin\left(2q_x a - q_y\frac{a}{2} + q_3\frac{a}{2}\right)\right] \\ F_x^I(2,\frac{1}{2},\frac{1}{2})\left[\sin\left(2q_x a + q_y\frac{a}{2} + q_3\frac{a}{2}\right) + \sin\left(2q_x a - q_y\frac{a}{2} - q_3\frac{a}{2}\right)\right] \\ F_y^I(2,\frac{1}{2},\frac{1}{2})\left[\sin\left(2q_x a + q_y\frac{a}{2} + q_3\frac{a}{2}\right) - \sin\left(2q_x a - q_y\frac{a}{2} - q_3\frac{a}{2}\right)\right] \\ F_3^I(2,\frac{1}{2},\frac{1}{2})\left[\sin\left(2q_x a + q_y\frac{a}{2} + q_3\frac{a}{2}\right) - \sin\left(2q_x a - q_y\frac{a}{2} - q_3\frac{a}{2}\right)\right] \end{pmatrix} \tag{B21}$$

$$\underline{\underline{G}}(\vec{q})_{\underline{\underline{VII}}} = \frac{2i}{N} \begin{pmatrix} F_x^I(1,\frac{3}{2},\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} + q_z \frac{3a}{2}\right) + \sin\left(q_x a - q_y \frac{3a}{2} - q_z \frac{3a}{2}\right)\right] \\ F_y^I(1,\frac{3}{2},\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} + q_z \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} - q_z \frac{3a}{2}\right)\right] \\ F_z^I(1,\frac{3}{2},\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} + q_z \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} - q_z \frac{3a}{2}\right)\right] \\ F_x^I(1,\frac{3}{2},-\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} - q_z \frac{3a}{2}\right) + \sin\left(q_x a - q_y \frac{3a}{2} + q_z \frac{3a}{2}\right)\right] \\ F_y^I(1,\frac{3}{2},-\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} - q_z \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} + q_z \frac{3a}{2}\right)\right] \\ F_z^I(1,\frac{3}{2},-\frac{3}{2})\left[\sin\left(q_x a + q_y \frac{3a}{2} - q_z \frac{3a}{2}\right) - \sin\left(q_x a - q_y \frac{3a}{2} + q_z \frac{3a}{2}\right)\right] \end{pmatrix} \tag{B22}$$