

THEORETICAL ANALYSIS OF THE TYPE I
 $F_A(\text{Na})$ AND TYPE II $F_A(\text{Li})$ CENTERS
IN KCl

A Thesis

submitted in partial fulfilment of
the requirements for the degree of

Doctor of Philosophy

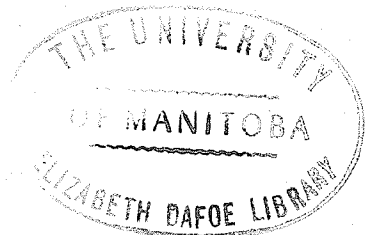
at

The University of Manitoba

by

Chong Kim Ong

March, 1973



ACKNOWLEDGEMENTS

The author would like to express his sincere thanks and deep appreciation to his supervisor, Dr. J.M. Vail, for his guidance throughout the course of the work. Dr. R.J. Brown's computer programs have been much appreciated.

ABSTRACT

Details of the electronic and ionic structure of the absorption energy and the ground and excited state reorientation energies of the $F_A(\text{Na})$ and $F_A(\text{Li})$ centers have been studied theoretically. The variational method is used to estimate the energy levels and wave functions, and one-parameter Gaussian-localized trial wave functions are used. The lattice is treated as unpolarizable point ions plus the ion-size correction arising from the approximate pseudopotential method developed by Bartram, Stoneham, and Gash. The lattice energy is the sum of the Coulomb interaction and the Born-Mayer repulsion, with Tosi's single exponential parameters as devised for perfect KCl, NaCl, and LiCl lattices. The lattice distortions and the electronic wave function are calculated self-consistently, using the method of lattice statics as modified for the case of an excess-electron defect with non-harmonic lattice distortion. The Franck-Condon principle is used for absorption and emission. The F_{A1} -absorption energy agrees with the experiment but with F_{A1} - F_{A2} splittings about three times too large. This discrepancy is probably largely due to ion-size correction. Energies of the relaxed excited state (RES) in vacancy and saddle-point configurations

are also estimated. The RES of $F_A(\text{Li})$ is found stabilized in the saddle-point configuration in agreement with experiment, but the $F_A(\text{Na})$ stabilization is wrong, although the error in the energy is less than 0.2 eV. Ground state reorientation energies agree with experiment for both centers. The role of the impurity cation in lowering the activation energies in both states is about equally divided between lattice energy and Coulomb electron-lattice interaction. Tentative results suggest that the saddle-point configurations for F- and F_A - centers may be quite different.

CONTENTS

	<u>Page</u>
Acknowledgements	(i)
Abstract	(ii)
Chapter 1 Introduction	1
1.1. Experimental Situation	3
1.2. Previous Theoretical Investigations	7
1.3. Brief Description of Our Model and Methods	10
1.4. Brief Summary of Our Results	11
1.5. Relevance of this Investigation	12
1.6. Brief Outline of Remainder of Thesis	14
Chapter 2 Methods and Model	15
2.1. The Lattice Energy	16
2.2. Franck-Condon Principles	16
2.3. Ion-size Correction	19
2.4. Method of Lattice Statics	28
(A) General Formulae	28
(B) Solution for ξ	33
(C) Energy Formulae	37
(i) The Relaxed State	37
(ii) Absorption Energy	38
(iii) Emission Energy	39

Chapter 3	Calculations, Results and Discussion	40
3.1.	Vacancy Configuration	42
	(A) Zeroth Order Calculation	42
	(B) Second Order Calculation	49
	(C) Absorption Energy	57
3.2.	Saddle-point Configuration	65
	(A) Zeroth Order Calculation	65
	(B) Second Order Calculation	68
	(C) Emission Energy	77
	(D) Investigation of the Stability of the Saddle- point Configuration	79
3.3.	Reorientation Activation Process	82
Chapter 4	Conclusions	87
References	92
Appendices	
	(A) Kellermann's Dynamical Matrix	95
	(B) Grouping of Ions for the Second Order Calculation . .	99
	(C) Block Diagram for the Computational Work for the Relaxed State	125

CHAPTER 1

INTRODUCTION

The main aim of the present work was to theoretically estimate the energy levels of $F_A(I)$ and $F_A(II)$ - centers⁽¹⁾ in KCl crystal, including both electronic transitions and the reorientation process. The type I or type II F_A - center in KCl is basically an F - center adjacent to a Na^+ or Li^+ substitutional impurity ion respectively (Fig. 1). The following physical parameters of these defects have been extensively studied:

- (1) Optical absorption energy;
- (2) Optical emission energy;
- (3) Activation energies for reorientation and dissociation.

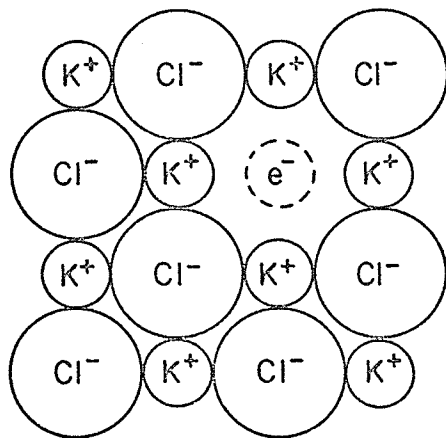
When the center has absorbed the photon, the bound excess-electron will be excited from its ground state to an excited state in a potential similar to the square well. The energy of the absorbed photon is called the absorption energy. The final state of the excess-electron in absorption, is called the unrelaxed excited state. The lattice then relaxes, until the excess-electron and the defect lattice are in mechanical equilibrium. This is called the relaxed excited state. The most striking single feature of

Figure 1

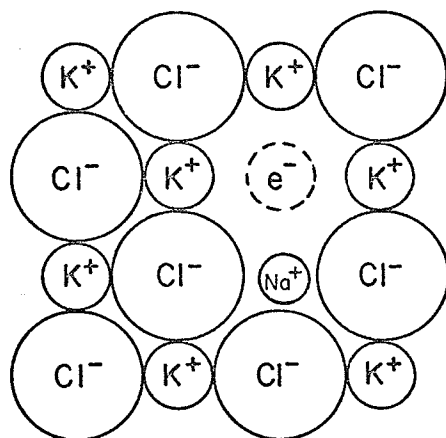
The ordinary F - center, $F_A(I)$ - center and $F_A(II)$ - center in KCl.

- (a) Ordinary F - center in KCl
- (b) $F_A(I)$ - center in KCl : Na
- (c) $F_A(II)$ - center in KCl : Li

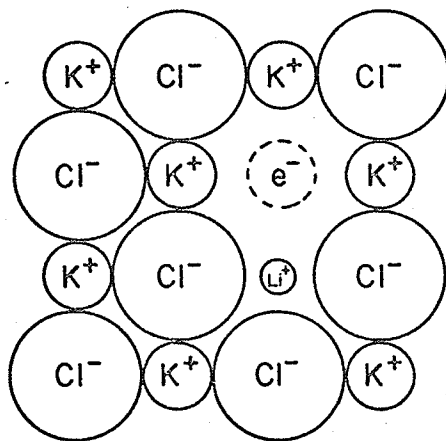
(a)



(b)



(c)



these centers occurs in the $F_A(II)$ - center, where the relaxed excited state is stabilized in the saddle-point configuration (Fig. 2b). In the saddle-point configuration, a negative ion lies half-way between two vacant anion sites. From the relaxed excited state, the emission process occurs and the final state of the optical emission process is the unrelaxed ground state. Again, the lattice relaxes to the equilibrium state, which is the relaxed ground state. In the reorientation process (Fig. 3), the F_A - center moves from one anion site to the nearest one which is adjacent to the impurity by the step-diffusion process, passing through the saddle-point configuration. In the dissociation process the F_A - center moves from one anion site to the nearest one which is not adjacent to the impurity.

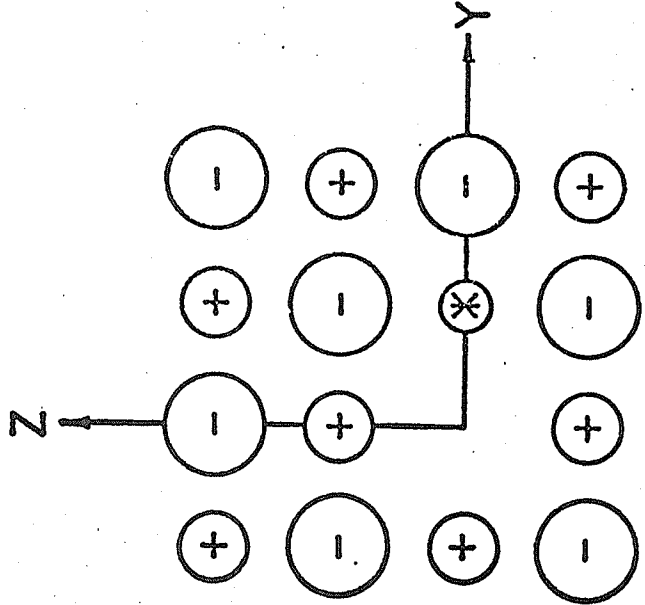
1.1 Experimental Situation

Experimentally, the three-fold degenerate F - center absorption transition has been observed to be split into two lines in the F_A - centers. This is due to reduction of the F - center's symmetry by the impurity cation. One of the absorption lines is polarized along the Z (or X) - axis, if the impurity cation is at (010), and is called the F_{A2} level (Fig. 4a), and the other is polarized along the y-axis (Fig. 4b), in the direction of the neighboring impurity cation, and is called the F_{A1} level. The position and shape of the emission band of the $F_A(Na)$ - center is similar to that of the F - center, but for the $F_A(Li)$ - center, it has a larger Stokes shift, a narrower emission band and the absence of thermal and field ionization of the excited state. Lüty⁽¹⁾ concluded that the emission processes occur in the vacancy configuration for the $F_A(Na)$ - center, and in the saddle point configuration for the $F_A(Li)$ - center. The experimental values for

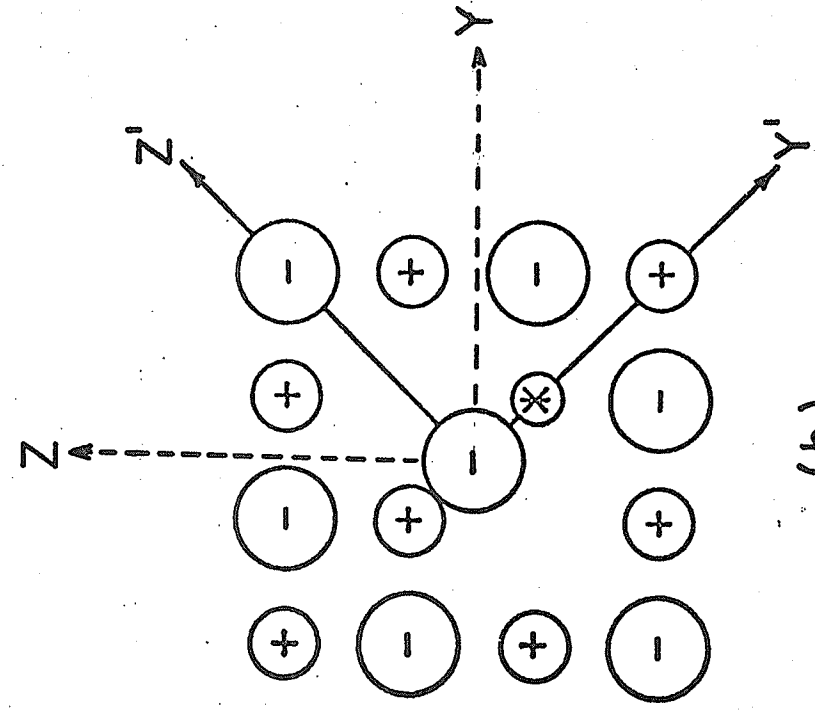
Figure 2

Vacancy and saddle - point configurations of the lattice for F_A - centers in KCl. \dagger denotes the cation, $-$ denotes the anion, and $*$ denotes the impurity substitutional cation.

- (a) vacancy configuration
- (b) saddle - point configuration



(a)



(b)

Figure 3

Model for reorientation of the F_A - center in KCl.

† denotes the K^+ ion, - denotes the Cl^- ion, * denotes the impurity cation and e^- denotes the trapped electron

- (a) initial state
- (b) intermediate state (saddle point configuration)
- (c) final state

(a)

+	-	+	-
-	+	-	+
+	e^-	*	-
-	+	-	+

(b)

+	-	+	-
-	+		+
+		*	-
-	+	-	+

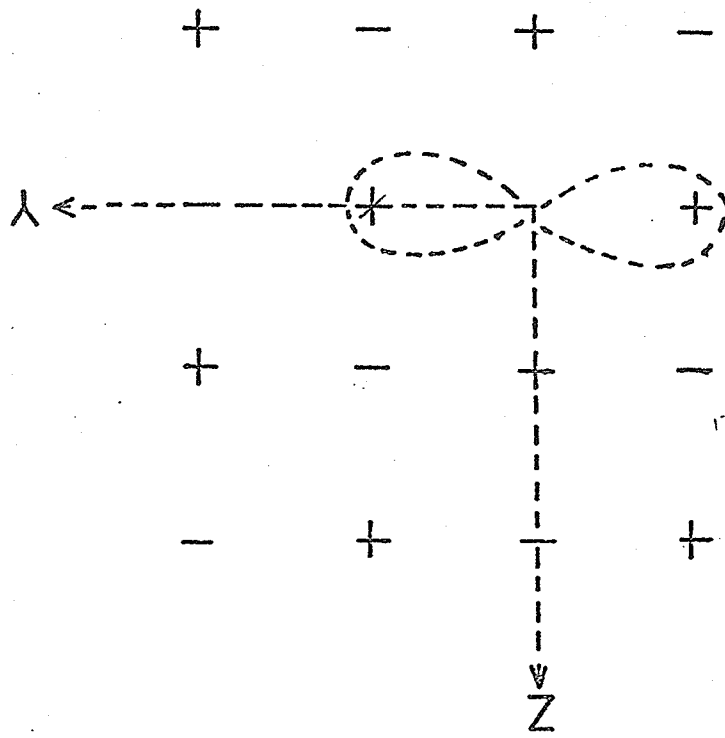
(c)

+	-	+	-
-	+	e^-	+
+	-	*	-
-	-	-	+

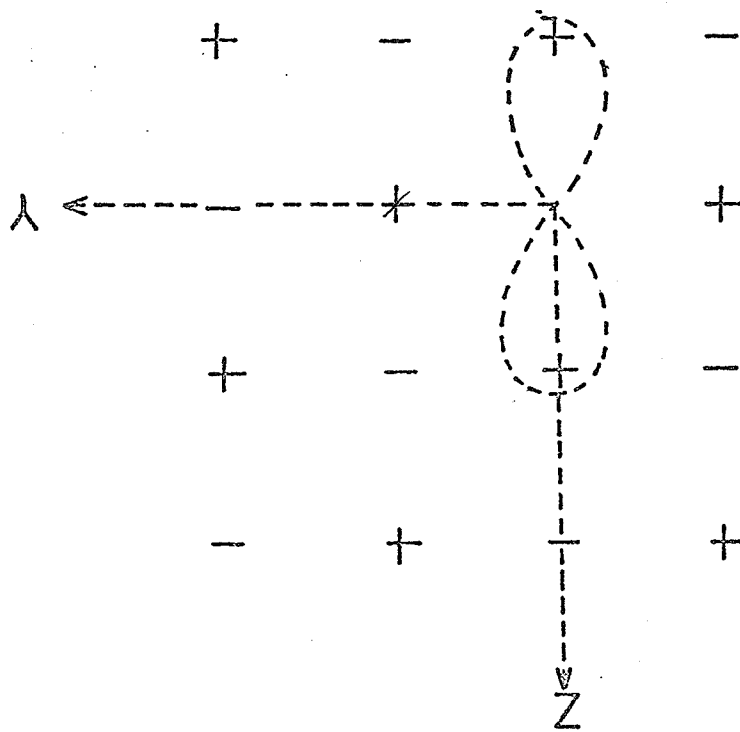
Figure 4

F_{A1} and F_{A2} unrelaxed excited states for F_A - centers in KCl. \dagger denotes K^+ ion, $-$ denotes Cl^- ion, $*$ denotes impurity ion, and $----$ schematically indicates excess - electron.

- (a) F_{A2} unrelaxed excited state
- (b) F_{A1} unrelaxed excited state



(a)



(b)

- (A) F_{A1} absorption energy;
- (B) $F_{A2} - F_{A1}$ absorption splitting;
- (C) even parity reorientation activation energy;
- (D) even parity relaxation energy in the saddle-point configuration;
- (E) emission energy in the saddle-point configuration;
- (F) odd parity reorientation activation energy

are shown in Figure 5. All the experimental data are taken from ref. (1). The energy levels relating to both vacancy configuration and saddle-point configuration are shown. The question marks in the figure means that the experimental values are not available.

The F_{A1} and F_{A2} transition measurements have been done by Lütty (ref. (1), p. 188) by optical methods. F_{A1} and F_{A2} absorption spectra can be observed by shining unpolarized light onto the crystal. The overlapping of the F_{A1} and F_{A2} spectra is decreased by using a dichroic crystal with suitable choice of polarization of the incident light. The reorientation process can be observed by the change in its F_{A1} or F_{A2} polarization on heating. Analysis of the temperature dependence of the relative absorption constant (ref. (1), p. 200) yields the reorientation energy.

1.2 Previous Theoretical Investigations

Three theoretical investigations of the absorption processes of both the $F_A(\text{Na})$ and $F_A(\text{Li})$ centers have previously been done (2), (3), (4). Two other investigations have studied $F_A(\text{Na})$ absorption only (5), (6). None of the authors attempt to verify the peculiar relaxed excited state of the $F_A(\text{Li})$ centers or the reorientation process for either center.

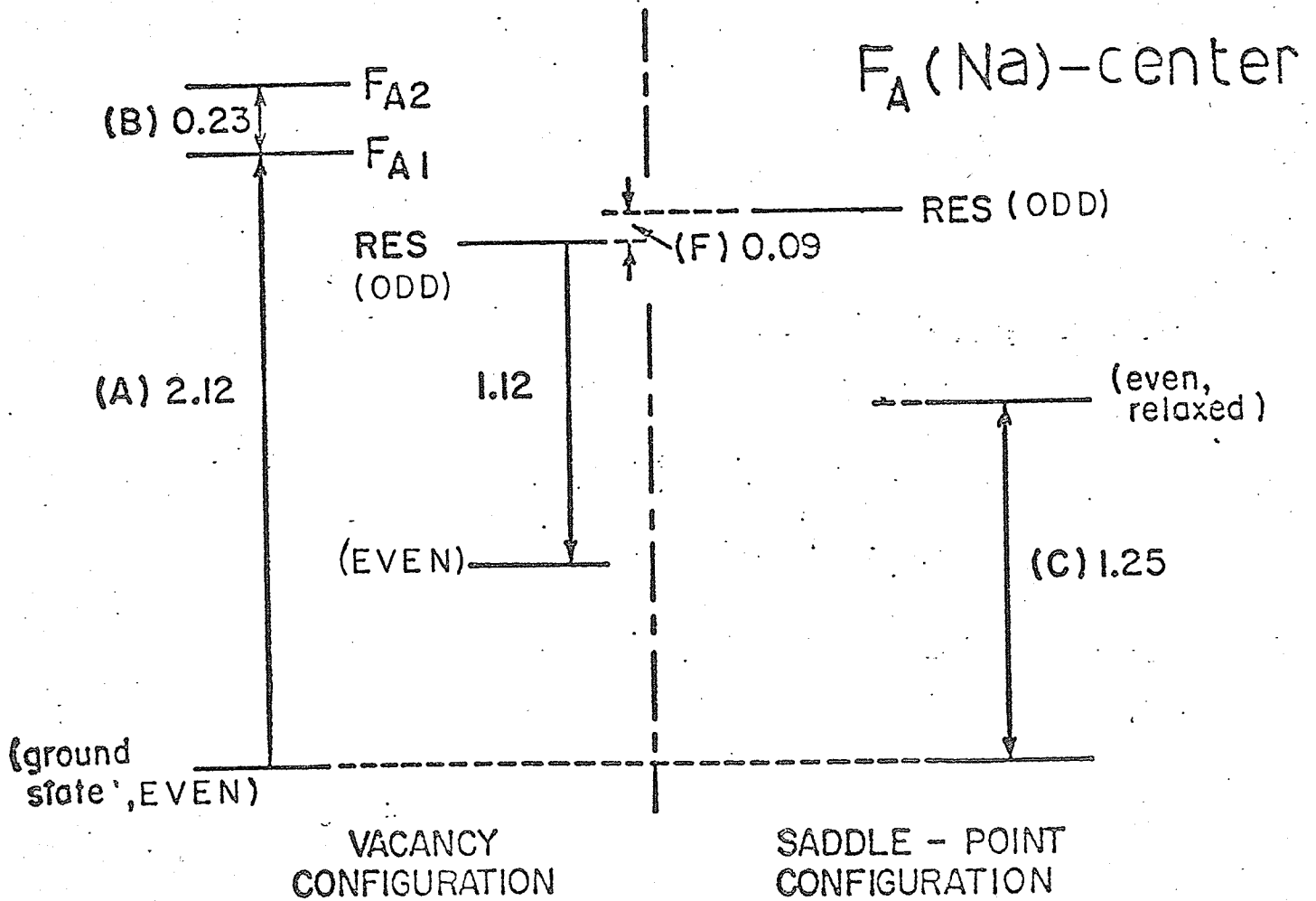
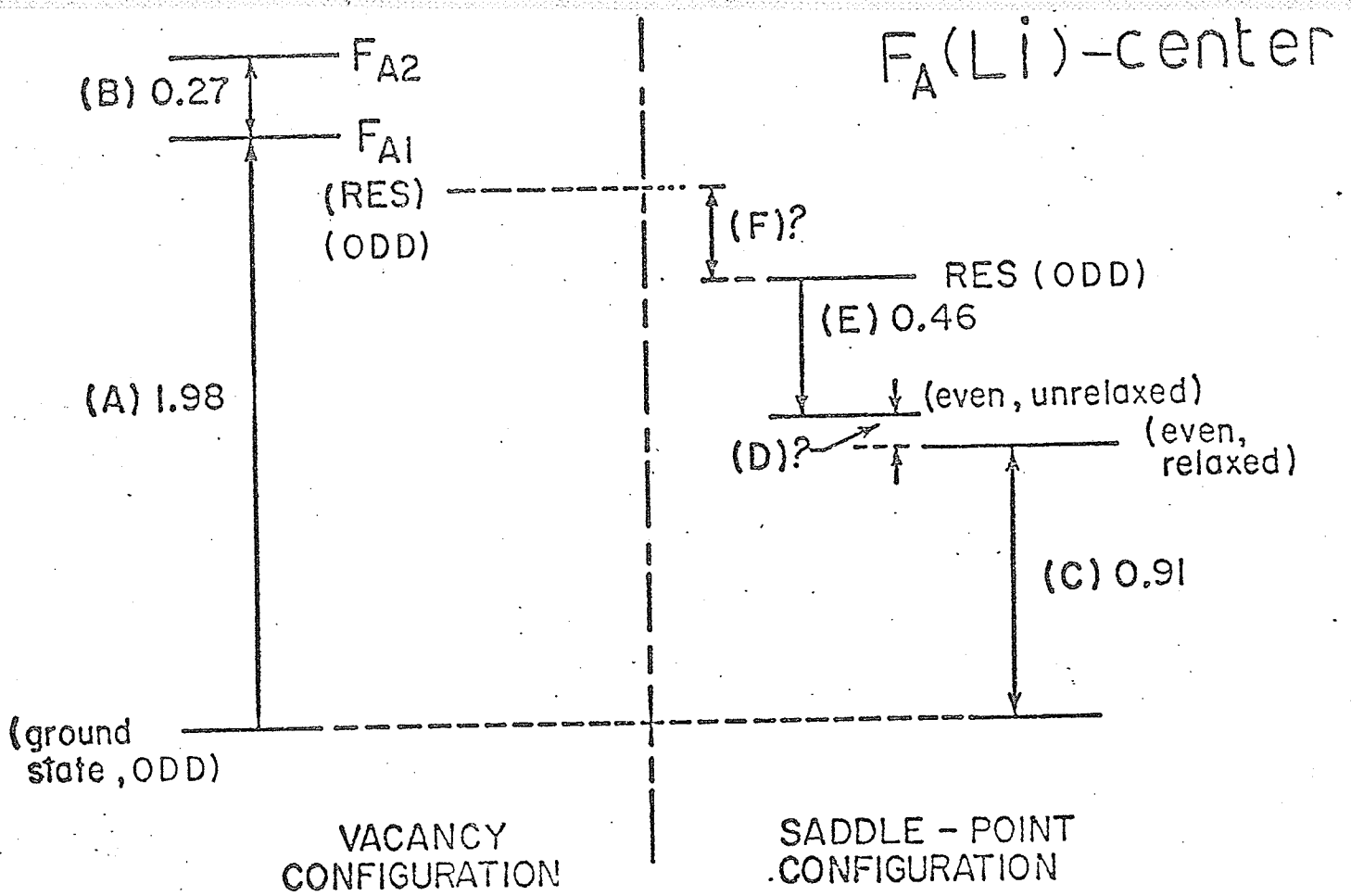
In order to understand the origin of the splitting, one has to go beyond the point ion approximation. The point ion lattice approximation has been used in an F - center absorption calculation by Gourary and Adrian (7). Their result is in moderate agreement with experiment. In the point ion lattice approximation, the ions are treated as point charges of appropriate sign. In other words, we neglect the size of the ion core; that is, we neglect the exchange interaction between the excess-electron and the core electron and the interaction of the excess F - electron with the point ion is taken to be purely electrostatic. Thus, the one electron Hamiltonian of the F - electron is the sum of the kinetic energy of the

Figure 5

Experimental energies (eV) for $F_A(\text{Li})$ and $F_A(\text{Na})$ - centers in KCl.

- (A) F_{A1} - absorption energy
- (B) $F_{A2} - F_{A1}$ absorption splitting
- (C) even parity reorientation activation energy
- (D) even parity relaxation energy in the saddle-point configuration
- (E) emission energy in the saddle point configuration
- (F) odd parity reorientation activation energy

The unlabelled energies 1.12 for $F_A(\text{Na})$ -center is the emission energy in the vacancy configuration.



F - electron and the electrostatic interaction of the F - electron and point ion lattice.

However, the electrostatic and exchange interactions between the excess-electron and the core electrons is important for the F_A - center study. Kojima et al⁽⁵⁾ used a linear combination of the atomic orbitals of the six nearest neighbors to the F_A - center as ground and excited state wave functions. They thus included the ion-size effect of the nearest neighbours and neglected the contribution from the other ions. They concluded that the energy differences between the unrelaxed F_{A1} - levels and unrelaxed F - levels are functions of the difference in ionization energy of the host and impurity cation. Smith⁽²⁾ has calculated the shift in the absorption energy between F and F_A - centers. He treated the difference of pseudopotentials of the nearest neighbour impurity cation and host cation as the perturbation on the point-ion approximation. The pseudopotential is determined from the requirement of the orthogonality of the F_A - center wave function to the core orbitals. Weber and Dick⁽³⁾ used the approximate pseudopotentials for the ion-size correction, as evaluated by Bartram et al⁽⁸⁾ (hereafter referred to as BSG), and which will be discussed further in Chapter 2. In order to get agreement with experiment, they discarded the reduction factor 0.53 which is suggested by BSG. Lattice distortion and ionic polarization are not included in their calculation.

⁽⁴⁾ Alig has developed an approximate form for ion size correction, similar to BSG, but without the reduction factor 0.53. He also included the lattice distortion and ionic polarization of the six nearest neighbours to the vacancy by the method of Gourary-Adrian⁽⁷⁾ (GA). GA - type wave functions have been used for the later three investigations but only Weber and Dick⁽⁴⁾ make them self-consistent with the lattice potential.

1.3 Brief Description of our Model and Method

In all previous investigations, and in the present-work, the lattice is considered as static, i.e. no dynamical effects are included. The adiabatic approximation⁽⁹⁾ is used to decouple the electronic state from that of the lattice. In the adiabatic approximation, the electron is assumed to move very fast in the potential provided by the lattice, and therefore follows the lattice motion adiabatically. On the other hand, the lattice cannot respond to the electron's instantaneous position, only to its average position. The Franck-Condon principle is also applied, which states that the transition of the electron from one state to another occurs while the lattice remains fixed. In fact, in some states the excess electron may interact with the optical phonon modes to behave like a polaron and such electron lattice interaction is non-adiabatic^{(10), (11)}.

Two main problems involved in point-defect calculations are:

- (1) to determine the appropriate interionic potential;
- (2) for a given potential, to calculate the distortion field about the defect.

For the F_A - center, one further problem has to be solved: the excess-electron wave function.

In the present work, the Born-Mayer potential with Tosi's single exponential parameters⁽¹²⁾ was used. That is, we used perfect lattice parameters for the defect lattice. This approximation seems to have been justified in Tosi's calculation⁽¹³⁾ of the vacancy migration energy in KCl. It remains to be seen how well justified it is in other defects.

The method we used in calculating the excess-electron wave function was variational. The trial wave functions which we used were Gaussian-localized, low-order Legendre polynomials. The ion-size effect has been

included by using BSG approximate pseudopotential with the reduction factor $\alpha = 0.53$. In this approximation, the pseudopotential introduces an extra term into the Hamiltonian. The justification for α has been discussed by Stoneham⁽⁴²⁾.

The displacements of the ions around the defect from their perfect lattice sites have been calculated and the resulting contribution to the defect system's energy has been included. The method which we used for this is called the lattice statics method^{(14),(15),(16)}, in which the whole lattice is treated as discrete and the results can be made exact within the harmonic approximation. The method has been extended by Vail⁽¹⁷⁾ to include non-harmonic lattice distortion near the defect. The criterion that we used for identifying the ions with non-harmonic displacements is that convergency of the solution of ξ failed if they were included in region II. (see equation (2.83) and appendix (c)). The further merit of this method is that the distortion field of the lattice is made self-consistent within the excess-electron wave function. There is no doubt that the wave function of the excess-electron will alter as the lattice distorts.

In short, our estimates of electronic defect energies are based on a variational procedure in which parameters in a trial electronic wave function and the ionic displacements are determined self-consistently to minimize the total energy of the system.

1.4 Brief Summary of our Results

Comparison of our calculated results with experiments show the following:

- (1) the even-parity reorientation energies of both $F_A(\text{Li})$ and $F_A(\text{Na})$ centers are in good agreement with experiment;
- (2) the F_{A1} absorption energy for both $F_A(\text{Li})$ and $F_A(\text{Na})$ centers, agrees with the experiment;
- (3) the relaxed excited state of $F_A(\text{Li})$ is stabilized in the saddle point configuration;

- (4) the splitting of $F_{A1} - F_{A2}$ absorption is about three times too large, compared with experiment.

Our results fail to describe:

- (1) the emission process of the $F_A(\text{Li})$ in the saddle-point configuration;
 (2) the relaxed excited state of $F_A(\text{Na})$ stabilized in the vacancy configuration.

Throughout the project, we refused to make any empirical correction to improve our agreement with the experiment, because this would hide the weakness of the model and method, which is one of our objectives to assess.

1.5. Relevance of this Investigation

There are three areas of relevance for this investigation:

(1) qualitative features

In the present investigation, the system's energy can be conveniently expressed in five parts: the electron's kinetic energy, the point ion potential, the ion-size correction, the lattice defect energy, and the harmonic lattice distortion energy. Thus, the role which the excess-electron plays in the step-diffusion process in both odd-parity and even-parity states, can be understood qualitatively. Also by comparison of the contribution from the different terms to the activation energy of the F_A - center and the ordinary F - center, the role of the impurity ion in the activation process can be qualitatively assessed.

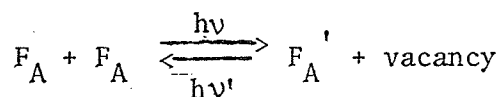
(2) theoretical relevance

The results of the present calculation will give some indication

of how well our model and approximations can describe the properties of defects. Discrepancies with experiment will give some indication of possible modifications and improvements which should be made to the model and methods.

(3) Applications

The F_A - center occurs in photochromic materials⁽¹⁸⁾ and therefore, has some relevance in design of photochromic devices. Photochromic materials are those which change color in a reversible way under illumination. The reversible photochromic process for F_A - center is



where $h\nu$ is the energy needed to ionize the F_A - center electron to the conduction band. The electron can then be trapped by another F_A - center to form an F_A' - center, the F_A' - center consisting of two electrons trapped in the anion vacancy. The position and sharpness of the F_A' - center lines are very different from those of the F_A - center. Similarly, one of the electrons of the F_A' - center can be ionized into the conduction band and be trapped by a vacancy to form another F_A - centers, giving the original configuration. Some of the factors which determine whether a photochromic device can be based on a given electronic defect, and which could be assessed using the present model and methods are:

- (1) the defect energy levels relative to the conduction band;
- (2) the relative magnitudes of the absorption energy for related but different defects (e.g. F_A and F_A' - center)
- (3) the presence or absence of competing absorption and emission

processes.

1.6. Brief Outline of Remainder of Thesis

The basic elements of our model and methods, namely, Tosi's single-exponential form of Born-Mayer repulsion, Franck-Condon approximation, the BSG ion size correction, and the method of lattice statics will be described and discussed in chapter 2. The details of the calculation and the results will be reported and analysed in chapter 3. This will include the energy levels and distortions for both relaxed and unrelaxed states in each of the two configurations. The role of the impurity ion in the activation process is also discussed. The critical assessment is given and suggestions are made in chapter 4.

CHAPTER 2

METHODS AND MODEL

The purpose of this chapter is to provide the theoretical background for the point defect calculation. In the present calculation, the lattice is treated as discrete point charges bound by Coulomb interaction and stabilized by a repulsive force. Tosi's single exponential form of Born-Mayer repulsion has been used. The ion-size effect of the lattice is taken care of by the BSG approximation with the empirical factor $\alpha = 0.53$, which is based on a pseudopotential method. For the electronic part of this problem, a one electron Hamiltonian is used. The variational method is used for calculating the electronic wave function and energy levels. In the variational method, the ion-size correction is just an extra term in the electronic Hamiltonian. For the lattice part of this problem, the lattice distortion is calculated rigorously by the lattice static method. Furthermore, the excess-electron wave function is not only made self-consistent with the given potential but also with the lattice distortion. However, ionic polarization and electron-phonon interaction are not included. The Franck-Condon approximation is used for calculating absorption and emission energy. In the following sections, we are going to discuss

(1) the lattice energy (2) the Franck-Condon approximation (3) the ion size correction and (4) the method of lattice statics.

2.1. The Lattice Energy

In the point ion model, the ionic interaction can be written as the sum of Coulomb (c) and repulsive (R) parts,

$$W = W^{(c)} + W^{(R)} \quad (2.1)$$

Tosi⁽¹²⁾ has developed a Born-Mayer type single exponential (SE) form for $W^{(R)}$;

$$W^{(R)} = B \exp \left(- \frac{r}{\rho} \right) \quad (2.2)$$

$W^{(R)}$ applies only to nearest neighbour interactions. The parameters B and ρ are determined from the following equations of state which included the temperature correction.

$$\frac{dW}{dV} = -p + \frac{T\beta}{K} \quad (2.3)$$

$$V \frac{d^2W}{dV^2} = \frac{1}{K} + \frac{T}{K^2} \left[\left(\frac{\partial K}{\partial T} \right)_p + \frac{\beta}{K} \left(\frac{\partial K}{\partial p} \right)_T \right] \quad (2.4)$$

where K is the isothermal compressibility and β is the volume coefficient of thermal expansion. The determined value of β and ρ have been given in ref. (12) table VII 2nd column. The SE form is known to give reasonable results for vacancy migration⁽¹³⁾.

2.2. Franck-Condon Principle

The following discussion of the Franck-Condon principle will be restricted to the static lattice model which we have used in the present

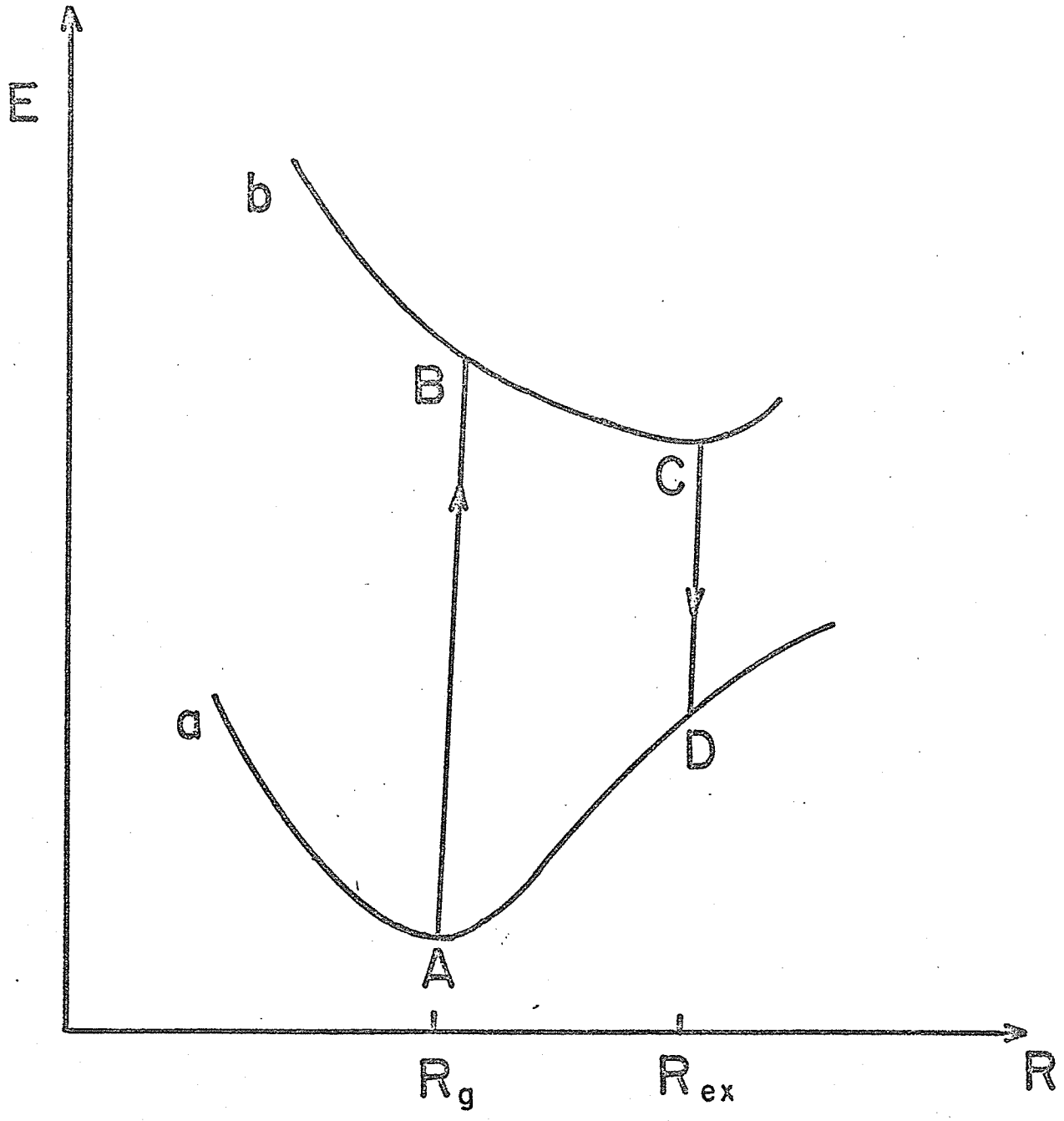
calculation.

There are two electronic bound states involved for each electronic transition considered in this work. For each of the electronic states, there is a different set of equilibrium lattice distortion parameters (μ, ξ) , because of the different charge distributions of the excess-electron interacting with the lattice. In order to describe the Franck-Condon principle for the transition of the electron from one state to the other, we are going to introduce the so-called "configuration coordinate" diagram. The configuration coordinate can be understood by reference to figure 6, where the defect system's energies are plotted as a function of a single coordinate, different values of which correspond to different lattice configurations. The lower curve of Fig. 6 is the energy curve corresponding to the electronic state a, or ground state. The upper curve is the energy curve for the electronic state b, or first excited state. The optical absorption and emission processes for the color center can be visualized from this configuration diagram, as follows. When F_A - center is in the ground state A, it will be excited to the first excited state B after absorbing a photon. Thereafter, the lattices has to readjust to the new charge density of the electron, and so it relaxes to C by giving up energy as phonons. The emission process occurs from state C. Again, the system relaxes from state D to state A by giving up the corresponding energy as phonons.

The configuration coordinates of the state A and B are the same, namely R_g in Fig. 6. Similarly, state C and state D have the same configuration coordinate R_{ex} . This is the essence of the Franck-Condon principle, which assumes that in the most probable transitions, the ionic coordinates do not change, or "vertical transitions" occur in the configur-

Figure 6

Configuration coordinate diagram for an F_A - center.
A \rightarrow B is the absorption process and C \rightarrow D is the
emission process, in Franck - Condon approximation.
E is the total defect system's energy and R is the
"configuration coordinate".



ation diagram. In short, in terms of the configuration coordinates, the Franck-Condon principle describes the absorption energy and emission energy as the magnitude of $A \rightarrow B$ and $C \rightarrow D$, as in Fig. 6, while the Stokes shift is described as the difference of the magnitudes $A \rightarrow B$ and $C \rightarrow D$.

The limits of validity of the Franck-Condon principle are not obvious. It depends on details of the phonon distribution and on the electron phonon interaction both of which are ignored in our treatment^{(10), (11)}.

2.3. Ion-size Correction

The following discussion on the ion-size correction is based on ref. (21).

Consider the Schrödinger equation

$$H \psi = E \psi \quad (2.5)$$

where $H =$ one electron Hamiltonian $= T + V$

$T =$ kinetic energy operator

$V =$ the potential energy due to all the ions, and the eigenfunction ψ of the excess-electron must be orthogonal to the core states $|c\rangle$ of the ions. Now, let us define $|\phi\rangle$ by

$$\begin{aligned} |\psi\rangle &= |\phi\rangle - \sum_c |c\rangle \langle c | \phi \rangle \\ &= (1 - \sum_c |c\rangle \langle c|) |\phi\rangle \end{aligned} \quad (2.6)$$

where $|\phi\rangle$ is a smooth wave function which is not orthogonal to the core state. Write

$$P = \sum_c |c\rangle \langle c| \quad (2.7)$$

which is known as the projection operator, projecting onto the core states.

Then, equation (2.6) becomes

$$|\psi\rangle = (1 - P) |\phi\rangle \quad (2.8)$$

In the pseudopotential method, instead of solving the eigenvalue equation (2.5) for ψ , one considers another eigenvalue problem

$$(H + V_R) \phi = \tilde{E} \phi \quad (2.9)$$

which is solved for ϕ , called the pseudo-wave function. Let us write

$$V_R = P O_p \quad (2.10)$$

where O_p is an arbitrary operator. There are two different forms of V_R which are of interest in color center calculations, namely:

(1) Cohen and Heine⁽¹⁹⁾ pseudopotential (V_p^{CH})

(2) Phillips and Kleinman⁽²⁰⁾ pseudopotential (V_p^{PK})

For V_p^{CH} operating with $(1 - P)$ from the left on equation (2.9) gives:

$$(1 - P) (H + V_R) \phi = (1 - P) \tilde{E} \phi \quad (2.11)$$

Making use of equation (2.10), $P^2 = P$ and $[H, P] = 0$, equation (2.11) becomes:

$$H(1 - P) \phi = \tilde{E} (1 - P) \phi \quad (2.12)$$

Therefore $(1 - P)\phi$ is a eigenfunction of H and we denote the eigenvalue $\tilde{E} = E$. Then, equation (2.9) can be written as

$$(T + V + P O_p) \phi = E \phi$$

or

$$(T + V_p) \phi = E \phi \quad (2.13)$$