Unrestricted Hartree-Fock Cluster Calculations
on F and F_A-Centres in Alkali Halides

by

Andrew Yum Sing Kung

A thesis
presented to the University of Manitoba
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
Department of Physics

Winnipeg, Manitoba, 1981

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CONTENTS

ABSTRACT

Ab-_initio_ unrestricted Hartree-Fock (UHF) calculations
are performed to study the electronic structures of some F-
and F_A-centres in alkali halides in the context of a cluster
model. The cluster consists of the F-centre and its six
nearest neighbours, while the rest of the crystal is simu-
lated by a regular array of point charges to give the cor-
rect Madelung potential. The optical absorption energies
and ground state hyperfine structure (hfs) parameters are
calculated. It is found that the UHF cluster method yields
accurate energetics in both the F- and F_A-centres (except
LiF), but fails to give reliable hfs parameters, probably
due to the neglect of second and possibly further nearest
neighbours. The effect of spin polarization is also esti-
mated. It is found to be quite significant in the lithium
halides, but not so important in the potassium halides.
Lattice distortion is ignored throughout, except in the case
of the F_A-centre in KCl:Li where the calculation is repeated
with the impurity Li^+ ion displaced outward from the vacancy
along the symmetry axis by 8% of the nearest neighbour spac-
ing. The results indicate that this does not alter the
qualitative features of the previous findings.

ACKNOWLEDGEMENTS

Chapter I

THE ION-SIZE EFFECT IN COLOUR CENTRE PROBLEMS

1.1   INTRODUCTION

Calculation of the electronic structures of point defects in ionic crystals is in the fifth decade. Despite zealous theoretical efforts, culminating in the 1960's, numerous challenging problems remained. Even today, the nature of the Relaxed Excited State, the coupling of the electronic states to phonons of the host lattice, distortion and polarization in the vicinity of the defect, are still wide open to theoretical investigation. Above all is the many-body aspect of the quantum mechanical system, which demands equivalent treatment of all electrons within the system. The present work addresses this problem. It is convenient to base the discussion on a specific defect. The F-centre, consisting of an electron trapped in an anion vacancy (see fig. 1a), has been treated extensively because of its simple structure and high-symmetry environment. Here, the excess electron is combined with the electronic structure of ions neighbouring the vacancy. (Throughout this work, the terms "F-electron" and "excess electron" will be used synonymously). In this context, the classification of "defect electrons" (the group of electrons which are most sensitive to

Fig. 1a: F-centre in KCl

1b: F_A-centre in KCl:Li

(+) : K^+ ion

(−) : Cl^- ion

⊕ : Li^+ ion

(e^-) : excess electron

Fig. 1a
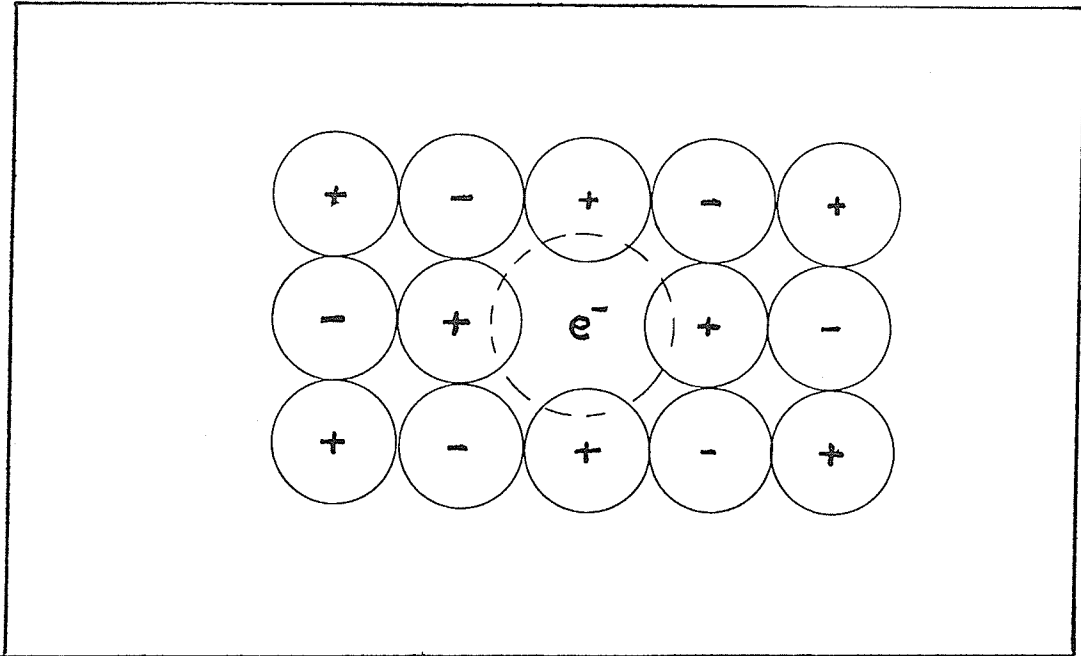
Fig. 1b
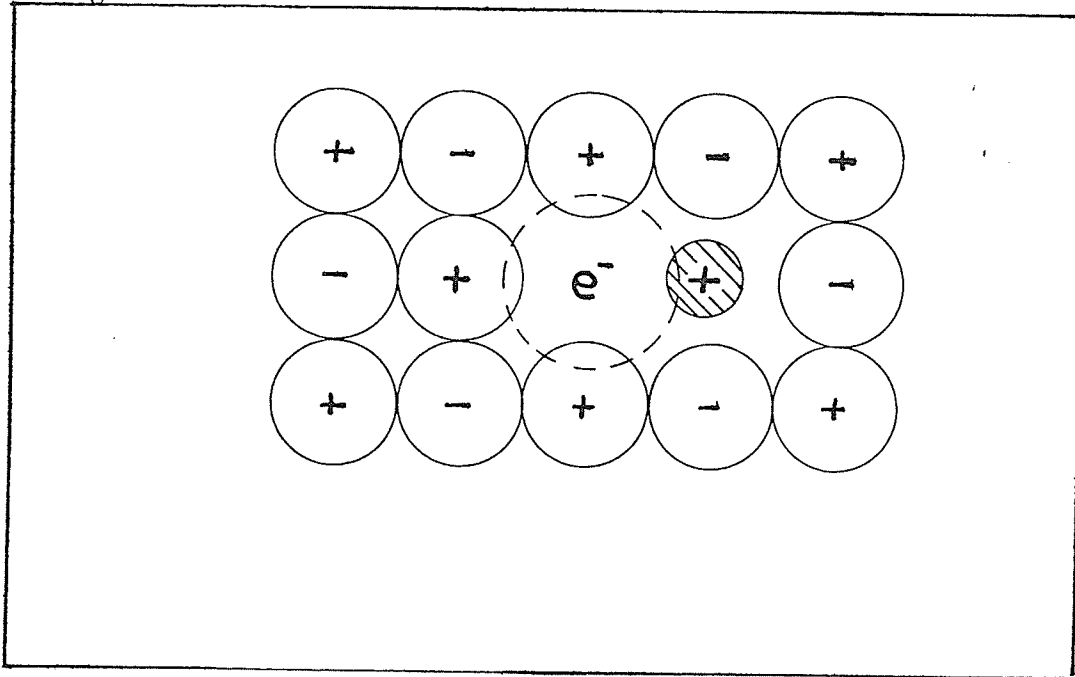
the perturbation due to the presence of the defect) and "core electrons" (electrons which do not feel the presence of the defect) is not rigorously correct. Nevertheless, for practical computational purposes, such a distinction is always made. Since one is primarily interested in defect properties which are overwhelmingly governed by the state of the defect electrons, they are treated as accurately as possible, while the core electrons are usually reduced to a fixed background potential and/or an additional constraint to which the defect electrons are subject. The term "Ion-Size Effect" in the literatures of colour centres refers to the effect of imposing the Pauli Exclusion Principle to the system rather than simply treating the ions as classical point charges.

The properties of various colour centres are reviewed in detail by Fowler[1] and by Stoneham[2]. Because of the large number of papers published on this subject, each with its own emphasis, it is desirable to have a quick review of a subset of these which have particular relevance to the ion-size effect. Special attention will be paid to the physical assumptions made in previous theoretical works. This will also serve to focus on the particulars of the theoretical model used in the present work, which will be described in detail in the next chapter.

1.2 BRIEF SURVEY OF PREVIOUS THEORETICAL PROCEDURES

Typically, there are three levels of sophistication involved in all the defect calculations. They are:

(1) The self-consistent readjustment of the core orbitals when the defect is introduced.

(2) The treatment of overlap among cores, and

(3) Overlap between excess electron orbitals and the cores.

Most previous calculations ignore Level 1, or treat it with some very simplifying assumptions, the justification being that a fully self-consistent treatment would raise the problem to an impossible computational level.

Levels 2 and 3 pose the problem of orthogonality, which has been widely considered. The orthogonality constraint is incorporated in some variational calculations, whereby the defect wavefunction is varied subject to this constraint to yield the minimum energy. There are two ways in which the constraint can be built into the calculation. These are referred to as the Extended Ion method and Pseudopotential method, and will be discussed under separate headings below. This does not exhaust all the possible theoretical methods. For example, there is an older class of calculation using the continuum and semi-continuum model, the details of which have been reviewed by Gourary and Adrian[3].

1.2.1   Extended Ion Method

In the Extended Ion method, one explicitly orthogonalizes the set of orbitals used through either the Schmidt procedure or Lowdin's method[4]. Although the two methods can be shown to be equivalent, the later is usually preferred because it offers a more systematic approach. Thus one starts with a set of orbitals $\{\phi_i\}$, which consists of atomic-like orbitals localized on different nuclear sites plus some trial wavefunction localized on the defect centre. Note that orbitals localized on different centres are non-orthogonal. One looks for a linear transformation, $\underline{\underline{A}}$, which transforms $\{\phi_i\}$ into $\{\tilde{\phi}_i\}$, such that each $\tilde{\phi}_i$ is mutually orthogonal and normalized:

$$\tilde{\phi}_i = \sum_j \phi_j A_{ij} \tag{1.1}$$

$$\int \tilde{\phi}_i \, \tilde{\phi}_j \, d\vec{r} = \delta_{ij} \tag{1.2}$$

The transformation matrix $\underline{\underline{A}}$ can be found by substituting (1.1) into (1.2). The requirement of orthonormality leads to:

$$\underline{\underline{A}}^+ \, \underline{\underline{S}} \, \underline{\underline{A}} = \underline{\underline{I}} \tag{1.3}$$

where $\underline{\underline{I}}$ is the identity matrix

$\underline{\underline{S}}$ is the overlap matrix defined by:

$$S_{ij} = \int \phi_i^* \, \phi_j \, d\vec{r}$$

$$= \delta_{ij} + \Delta_{ij} \tag{1.4}$$

δ_{ij} in (1.4) is the Kronecker delta and Δ_{ij} is the non-diagonal element of $\underline{\underline{S}}$. The solution of $\underline{\underline{A}}$ in (1.3) is:

$$\underline{\underline{A}} = \underline{\underline{S}}^{-1/2}\,\underline{\underline{U}} \tag{1.5}$$

with

$$\underline{\underline{U}}^{+}\,\underline{\underline{U}} = \underline{\underline{I}},$$

and $\underline{\underline{U}}$ is arbitrary otherwise. The arbitrariness in $\underline{\underline{U}}$ is equivalent to the arbitrariness one obtains in choosing the starting vector in the Schmidt procedure. If one chooses:

$$\underline{\underline{U}} = \underline{\underline{I}}$$

then

$$\underline{\underline{A}} = \underline{\underline{S}}^{-1/2}$$

$$\tilde{\phi}_i = \sum_j \phi_j \left(\underline{\underline{S}}^{-\frac{1}{2}} \right)_{ji} \tag{1.6}$$

(1.6), as it stands, is exact. However, the elements of $\underline{\underline{S}}^{-1/2}$ are difficult to evaluate. Noting that the overlap amongst orbitals on different centres is small, $\underline{\underline{S}}^{-1/2}$ is expanded in power series:

$$\underline{\underline{S}}^{\frac{1}{2}} \equiv \left(\underline{\underline{I}} + \underline{\underline{\Delta}} \right)^{-\frac{1}{2}} = \underline{\underline{I}} - \frac{1}{2}\underline{\underline{\Delta}} + \frac{3}{8}\underline{\underline{\Delta}}^2 - \cdots \tag{1.7}$$

and (1.6) becomes:

$$\tilde{\phi}_i = \phi_i - \frac{1}{2}\sum_j \phi_j \Delta_{ji} + \frac{3}{8}\sum_{jk}\phi_j \Delta_{jk}\Delta_{ki} - \cdots \tag{1.8}$$

Different extended ion calculations in the past hinge on the different ways with which the series (1.8) is treated. The accuracy of the various subsequent approximations had been assessed and discussed by Harker[5].

The starting set of orbitals, $\{\phi_i\}$, can be divided into two subsets $\{\phi_{\nu j}; \phi_F\}$ with $\phi_{\nu j}$ denoting the j-th core orbital localized on site ν and ϕ_F denoting the wavefunction of the F-electron. In neglecting the self-consistent readjustments of the cores, $\{\phi_{\nu j}\}$ is fixed (e.g. free Hartree-Fock orbitals from Clementi[6]), while ϕ_F becomes the trial wavefunction. Notice that, already at this level, the problem has been reduced to a one-electron variational one. Further, for computational reasons, usually only the six nearest neighbours (N.N.) of the F-centre are taken explicitly into account; that is, ν only runs from 1 to 6 in $\{\phi_{\nu j}\}$.

Successive levels of approximations are summarized below:

(a) Neglecting the overlaps between <u>all</u> the orbitals. This is equivalent to taking the first term of the expansion (1.8) only:

$$\tilde{\phi}_i \approx \phi_i$$

it means that all ion-size effects are ignored and the calculation reduces to the famous Point-Ion model of Gourary and Adrian[7]. The host crystal lattice becomes a regular array of point charges of ± 1 unit, which forms the potential in which the single F-electron moves. Apart from the variational solution by the above authors, this problem has been solved exactly by Laughlin[8].

(b) Neglecting core-core overlaps (amongst $\phi_{\nu j}$ for different ν) but including defect-core overlaps (between ϕ_F and $\phi_{\nu j}$).

Most of the extended-ion work is done at this level. Gour-
ary and Adrian[7] were the first authors to point out the
inadequacy of the Point-Ion model in calculating the hyper-
fine structure (hfs) constants,[1] since there is substantial
penetration of the F-wavefunction into the regions normally
occupied by the neighbouring cores. They suggested the
proper wavefunction Ψ_F to use in hfs calculations is one ob-
tained by orthogonalizing ϕ_F to the core orbitals $\phi_{\nu j}$ for
the hfs constant at site ν. Thus:

$$\Psi_F = N^{-1/2} \left\{ \phi_F - \sum_{j=1}^{N_\nu} \langle \phi_{\nu j} | \phi_F \rangle \phi_{\nu j} \right\} \qquad (1.9)$$

where N_ν is the number of core orbitals localized

on ν,

N is the Normalization constant

$$= 1 - \sum_{j=1}^{N_\nu} | \langle \phi_{\nu j} | \phi_F \rangle |^2$$

The overlap integrals in (1.9) are tedious to evaluate.
Since only $\Psi_F(R_\nu)$, where R_ν is the distance of the ν-ion
from the origin where the F-centre is located, is required,
Gourary and Adrian made a further approximation by neglect-
ing the variation of ϕ_F over the core region. Thus:

$$\langle \phi_{\nu j} | \phi_F \rangle \phi_{\nu j}(R_\nu) = \phi_{\nu j}(R_\nu) \int d\vec{r}\, \phi_{\nu j}^*(\vec{r})\, \phi_F(\vec{r})$$

----

[1] For a good review on the hfs of ESR and ENDOR spectra, see
ref. 9.

$$\approx \phi_{\nu j}(R_\nu)\, \phi_F(R_\nu) \int d\vec{r}\; \phi_{\nu j}^*(\vec{r})$$

$$= B_{\nu j}\, \phi_F(R_\nu)$$

where $\quad B_{\nu j} = \phi_{\nu j}(R_\nu) \int d\vec{r}\; \phi_{\nu j}^*(\vec{r})$ $\qquad$ (1.10)

Substituting this into (1.9), one obtains

$$\Psi_F(R_\nu) = G_\nu\, \phi_F(R_\nu) \qquad\qquad (1.11)$$

where $\quad G_\nu = N'\left[1 - \sum_{j} B_{\nu j}\right]$

$$N' = \left[1 - \phi_F(R_\nu) \sum_{j} \int d\vec{r}\; \phi_{\nu j}^*(\vec{r})\right]^{-1/2}$$

G_ν in (1.10) is referred to as the "Amplification Factor", which gives a one-to-one correspondence between the smooth F-wavefunction ϕ_F and the true wavefunction Ψ_F . It depends on the type of ion alone and can be calculated once and for all.

Even with the amplification factor introduced, there is still no ion-size effect in the energy level calculations because the orthogonalization is done after the optimization of ϕ_F . To be more rigorous, the variational calculation should start with a trial wavefunction (twf) which is explicitly orthogonalized:

$$\Psi_F(\vec{r}, \underline{\lambda}) = N^{-1/2}\left\{\phi_F(\vec{r}, \underline{\lambda}) - \sum_{\nu j} \langle \phi_{\nu j} | \phi_F \rangle\, \phi_{\nu j}\right\} \qquad (1.12)$$

where N is the normalization constant and $\underset{\sim}{\lambda}$ is a set of variational parameters. The Amplification Factor approximation has to be given up. Work along this line was carried out by Kojima[10][11] (on LiF), Wood and Korringa[12] (on LiCl), and Wood and Joy[13] (on all rocksalt-structured alkali halides except the rubidium and iodine salts). In Kojima's work on LiF, the Coulomb and exchange effect of the F-electron with its six Li^+ N.N. were included, whereas in Wood and Joy, only the outer shell of electrons of the six N.N. were included in Na^+ and K^+. Even at this level, (one-electron variational, free ion Hartree-Fock core orbitals constituting a background potential), as Wood and Joy remarked, the computations become very difficult to handle.

Further developments on extended-ion model calculations have been made by Opik and Wood[14] and Wood and Opik[15]. There are far more details in these two papers than can be accommodated here. However, there are three outstanding features, which are stated qualitatively below:

(i) The non-local exchange operator is replaced by an angular- momentum dependent, numerical, potential.

(ii) The N.N. ions are treated explicitly with the model potential as derived in (i) while the more distant ions are taken into account by Effective Mass Theory.

(iii) Polarization corrections are made empirically for the distant ions.

Recently, Leung and Song[16] also did an extended-ion calculation on the F-centre in LiF. Coulomb and exchange effects are included up to the fifth shell of neighbours. Their work differs from the previous ones by employing Gaussian-type orbitals (GTO), and fully exploiting the symmetry of the defect. They have also studied the effect of using different sets of core orbitals and concluded that the results are quite sensitive to the choice.

(c)   Including first-order core-core Overlaps.

Expansion (1.8) is kept up to the first order term:

$$\tilde{\phi}_i \approx \phi_i - \frac{1}{2} \sum_j \phi_j \Delta_{ji}$$

Wood[17] had calculated isotropic hfs constants up the eighth neighbours of the F-centre in KCl with this approximation. A critique on the accuracy of the calculation is found in Harker[5].

(d)   Exact inversion of the overlap matrix $\underline{\underline{S}}$.

Harker[18] has generated sets of orthonormal core orbitals $\{\tilde{\phi}_{vj}\}$ by evaluating $\underline{\underline{S}}^{-1/2}$ exactly, but they are used in conjunction with the pseudopotential method, which will be described in the next section.

1.2.2   Pseudopotential Method

The following discussion on pseudopotential theory follows section 6.2.4, Chapter 6 of Ref. 2. While the orthogonality constraint is included in the trial wavefunction explicitly in the extended-ion method, it is absorbed into the

Hamiltonian as an extra term in the pseudopotential approach. Thus, instead of solving:

$$\mathcal{H}\, \Psi_F \equiv (T + V)\, \Psi_F = E_F\, \Psi_F \qquad (1.13)$$

with
$$\Psi_F = \phi_F - \sum_c \langle \phi_c \mid \phi_F \rangle\, \phi_c \qquad (1.14)$$

where ϕ_c stands for a set of core orbitals (mutually orthogonal either through the application of the Lowdin procedure described before or through the approximation of neglecting core-core overlaps) and T and V are the kinetic and potential energy operators repectively, one considers:

$$(\mathcal{H} + V_R)\, \phi_F = (T + V + V_R)\, \phi_F$$

$$\equiv (T + V_P)\, \phi_F = \widetilde{E}_F\, \phi_F \qquad (1.15)$$

In (1.15), V_R is an (as yet unknown) potential term to simulate the requirement of orthogonality. V_P and ϕ_F are called the pseudopotential and pseudowavefunction respectively, while $\widetilde{E}_F$ is the corresponding eigenvalue. To correlate (1.13) with (1.15), it is convenient to introduce a projection operator P which projects a given function onto the manifold spanned by the core functions ϕ_c:

$$P = \sum_c \mid \phi_c \rangle \langle \phi_c \mid \qquad (1.16)$$

If ϕ_c's are mutually orthogonal, P is also idempotent:

$$P^2 = P \qquad (1.17)$$

In terms of P, the true wavefunction Ψ_F is related to the pseudowavefunction ϕ_F through

$$\Psi_F = (1 - P)\phi_F \qquad (1.14a)$$

The pseudopotential theorem asserts that if V_R in (1.15) is taken as:

$$V_R = P\Omega \qquad (1.18)$$

where Ω is an arbitrary operator. Then:

$$\widetilde{E}_F = E_F \qquad (1.19)$$

The proof can be obtained by substituting (1.18) into (1.15), and operating on both sides of the resulting equation with $(1 - P)$:

$$(1 - P)(\mathcal{H} + P\Omega)\phi_F = (1 - P)\widetilde{E}_F\phi_F$$

$$(\mathcal{H} + P\Omega - P\mathcal{H} - P^2\Omega)\phi_F = \widetilde{E}_F(1 - P)\phi_F$$

Using (1.17) and (1.14a) and assuming $\mathcal{H}$ commutes with P,

$$\mathcal{H}\Psi_F = \widetilde{E}_F\Psi_F$$

giving $\widetilde{E}_F = E_F$, which completes the proof. Thus, solving the constrained problem (1.13) and the unconstrained problem (1.15) yields the same energy E_F. The true wavefunction Ψ_F can be obtained from the pseudowavefunction ϕ_F through (1.14a).

The commutativity between $\mathcal{H}$ and P, which is assumed in the proof, needs to be examined. If ϕ_c are exact eigenstates of $\mathcal{H}$, the commutativity follows automatically. How-

ever, since one is primarily concerned with defect problem where $\mathcal{H}$ is the Hamiltonian of a crystal containing a defect, while ϕ_c is usually chosen as some free Hartree-Fock core orbitals, the commutativity is not exact. Nevertheless, such an approximation is always made. This amounts to neglecting core readjustment caused by the perturbation due to the crystal lattice and the defect. As described in the previous section, the same assumption is made in the extended-ion calculations too.

V_R as given in (1.18) is a repulsive potential. Inside the cores, there is large cancellation between V_R and the nuclear attractive potential, resulting in a relatively weak pseudopotential V_P (= $V + V_R$). This fact is often referred to as the "Cancellation Theorem". The smallness of V_P justifies the use of perturbation theory, which then explains the success of the nearly-free-electron model, and fast convergence of the orthogonalized-plane-wave method, and thus the pseudopotential method has lent itself to wide applicability in energy band calculations in metals[19]. In defect theory, however, it is the arbitrariness of V_R (through the arbitrary operator Ω) that renders this method useful. This arbitrariness can be exploited to satisfy certain key criteria in the problem. Accordingly, there are three common forms of pseudopotential, arising from different choices of Ω :

(a) Phillips-Kleinman form[20], V_P^{PK}:

$$V_P^{PK} = V + P\Omega^{PK}$$

with $\qquad \Omega^{PK} = (E_F - \mathcal{H})$ $\qquad$ (1.20)

This form is obtained by direct substitution of (1.14) into (1.13), first derived by Phillips and Kleinman, whose primary objective was to demonstrate the Cancellation Theorem. Consequently, the arbitrariness of V_R is not exploited. It is retained in the pseudowavefunction ϕ_F in that if ϕ_F is a solution to the eigenvalue problem (1.15), then, any ϕ_F', given by:

$$\phi_F' = \phi_F + \sum_c \alpha_c \phi_c \qquad\qquad (1.21)$$

is an equivalent solution for any α_c. This fact can readily be seen by noting that adding V_R to $\mathcal{H}$ raises all the core state eigenvalues E_c to a level which is degenerate with E_F. Thus,

$$(\mathcal{H} + V_R^{PK}) \phi_c = \tilde{E}_c \phi_c$$

$$[\mathcal{H} + P(E_F - \mathcal{H})] \phi_c = \tilde{E}_c \phi_c$$

Using $\mathcal{H} \phi_c = E_c \phi_c$ and $P = \sum_c |\phi_c\rangle\langle\phi_c|$,

$$\mathcal{H} \phi_c + \sum_{c'} (E_F - E_{c'}) |\phi_c\rangle\langle\phi_{c'}|\phi_c\rangle = \tilde{E}_c \phi_c$$

$$\tilde{E}_c = \langle \phi_c | \mathcal{H} | \phi_c \rangle + \sum_{c'} (E_F - E_{c'})\langle\phi_c|\phi_{c'}\rangle\langle\phi_{c'}|\phi_c\rangle$$

Using the orthogonality amongst the ϕ_c's, one gets:

$$\tilde{E}_c = E_F$$

Since any linear combinations amongst degenerate solutions are equivalent solutions, (1.21) follows.

(b) Cohen and Heine form[21] V_P^{CH}:

$$V_R^{CH} = P \, \Omega^{CH} = P \, (\bar{V} - V) \tag{1.22}$$

where $\quad \bar{V} = \langle \phi_F \mid V \mid \phi_F \rangle / \langle \phi_F \mid \phi_F \rangle \tag{1.23}$

The Cohen and Heine form is obtained by requiring that the pseudowavefunction ϕ_F be as "smooth" as possible. Mathematically, this requirement is met by minimizing the associated kinetic energy, or by requiring maximum cancellation between V and V_R, in which case the functional $\langle \phi_F \mid V + V_R \mid \phi_F \rangle / \langle \phi_F \mid \phi_F \rangle$ is minimized:

$$\delta \left\{ \frac{\langle \phi_F \mid V + V_R \mid \phi_F \rangle}{\langle \phi_F \mid \phi_F \rangle} \right\} = 0$$

$$\langle \delta \phi_F \mid V + V_R \mid \phi_F \rangle - \bar{V} \langle \delta \phi_F \mid \phi_F \rangle = 0 \tag{1.24}$$

Where $\bar{V}$ is given by (1.23). (1.24) must be true for arbitrary variation $\delta \phi_F$ equal to any core admixture as given in (1.21). Therefore,

$$\langle \phi_c \mid V + V_R \mid \phi_F \rangle - \bar{V} \langle \phi_c \mid \phi_F \rangle = 0$$

$$\langle \phi_c \mid V \mid \phi_F \rangle + \langle \phi_c \mid P\Omega^{CH} \mid \phi_F \rangle - \bar{V} \langle \phi_c \mid \phi_F \rangle = 0$$

Noting $\quad P \mid \phi_c \rangle = \mid \phi_c \rangle$

$$\langle \phi_c \mid \Omega^{CH} \mid \phi_F \rangle = \bar{V} \langle \phi_c \mid \phi_F \rangle - \langle \phi_c \mid V \mid \phi_F \rangle$$

from which (1.22) follows. Two things to note about V_P^{CH} are that, first, it is not Hermitian (through the presence of P) and second, it involves $\bar{V}$, the expectation value of V evaluated at the optimum ϕ_F, which means that self-consistent treatment is necessary.

(c) The Austin, Heine and Sham[22] form V_P^{AHS}:

$$V_R^{AHS} = P\Omega^{AHS} = -P \ V \qquad (1.25)$$

The Cohen and Heine form V_P^{CH} is sometimes referred to as the optimum pseudopotential in the sense that it gives the smoothest ϕ_F, but it carries with it the term $\bar{V}$ which is difficult to treat. Austin et.al. showed that V_R^{AHS} as given in (1.25) is also a valid form of pseudopotential which does not carry the term $\bar{V}$, but V_R^{AHS} is no longer optimum. The usefulness of V^{AHS} obviously depends on how important the criterion of "smoothness" is in the particular calculation.

The first rigorous pseudopotential calculation on F-centres was by Kübler and Friauf[23], who had used the Austin Heine and Sham form. We shall not go into the contents of this work because many of the essential features there are retained or improved in a later calculation due to Bartram, Stoneham and Gash[24] (BSG), which is reported below.

BSG used the Cohen and Heine form of pseudopotential. They defined a correction term, V_{IS}, due to ion-size effect as the deviation from the point-ion lattice potential V_{PI}:

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

$$= V_{PI} + V_{IS} \qquad (1.26)$$

where $\quad V_{IS} = (V - V_{PI}) + P(\bar{V} - V) \qquad (1.27)$

V in (1.27) is the Coulomb and exchange potential using free Hartree-Fock core orbitals. To evaluate the expectation value of V_{IS}, two further assumptions are made:

(i)   Neglect core-core overlaps

(ii)   Neglect the variation of the pseudowavefunction ϕ_F over the cores.

Assumption (i) enables one to write:

$$P = \sum_{\nu} P_{\nu}$$

$$V = \sum_{\nu} V_{\nu}$$

$$V_{PI} = \sum_{\nu} V_{PI,\nu}$$

where the summations are over the individual cores in the lattice. Substituting these into (1.26) and after some re-arrangement:

$$V_P = V_{PI} + \sum_{\nu} \left[(1 - P_{\nu})(V_{\nu} - V_{PI,\nu}) \right.$$
$$\left. - P_{\nu} V_{PI,\nu} + P_{\nu}(\bar{V} - U_{\nu}) \right]$$

where $\quad U_{\nu} = \sum_{\nu' \neq \nu} V_{\nu'} \approx \sum_{\nu' \neq \nu} V_{PI,\nu'}$

With assumption (ii), one arrives at the final form:

$$V_P = V_{PI} + \sum_{\nu} C_{\nu} \delta(\vec{r} - \vec{R}_{\nu}) \qquad (1.28)$$

where $\quad C_{\nu} = A_{\nu} + (\bar{V} - U_{\nu}) B_{\nu} \qquad (1.29)$

$$A_{\nu} = (1 - P_{\nu})(V_{\nu} - V_{PI,\nu}) - P_{\nu} V_{PI,\nu}$$

$$B_{\nu} = P_{\nu}$$

A_ν and B_ν as given in (1.29) depend only on the ionic species while U_ν depends only on the symmetry of the crystal lattice. Thus, given a set of core orbitals, these coefficients can be evaluated once and for all. BSG have tabulated the values of these coefficients for a wide variety of ionic species. When applying them to calculate the absorption energies of F-centres, however, they found that, in order to have reasonable agreement with experiment, the coefficient A_ν has to be multiplied by a numerical factor $\alpha = 0.53$.

Later, Harker[18] carried out an extensive study on the optical and magnetic properties of F-centres based on the BSG method but with assumption (i) (neglect core-core overlaps) removed. While the F-absorption energies are better than the corresponding point-ion model results, the hfs parameters do not show such improvement. Ong and Vail[26] have also studied the F-absorption energies by the BSG method with Kanzaki type of lattice relaxation around the defect.

While the empirical factor $\alpha = 0.53$ works well with F-centres, it cannot be applied to other defects such as F_A-centres. An F_A-centre is an F-centre with an adjacent substitutional cation impurity (see fig. 1b). Luty[27] has given a detail review of its properties. This centre is particularly interesting in the context of ion-size effects because the reduced symmetry due to the presence of the im-

purity splits the triply degenerate p-like excited state of the F-electron into two levels, one with symmetry axis parallel to the defect axis, and the other, which is doubly degenerate, with symmetry axis perpendicular to it. The transitions from the ground state to the former and latter are called F_{A1} and F_{A2} respectively (see fig. 2). In the point-ion lattice model, neglecting lattice relaxation, an F_A-centre is indistinguishable from an F-centre. Thus, the magnitude of the splitting between the F_{A1} level and the F_{A2} level becomes a very sensitive test of theoretical models designed to treat ion-size effects. Weber and Dick[28] have applied the BSG method directly to calculate the $F_{A1}-F_{A2}$ splittings while Alig[29] has used a slightly modified but basically equivalent form, with rough estimates of distortion and polarization corrections. They both came to the same conclusion, that with $\alpha = 0.53$, the splittings turned out in the wrong direction (The F_{A2} level being lower than the F_{A1}, which is contrary to experimental fact). When α is set to unity (no empirical correction), the splittings are in the right direction but the magnitude is much larger than is observed experimentally. Ong and Vail[30] have also made systematic calculations on the $F_{A1}-F_{A2}$ splittings, with more refined treatment of lattice distortion while Vail and Harker[31] have made a systematic study on the effect of using symmetry-adapted trial wavefunctions. Their findings reinforced the abovementioned conclusion.

Fig. 2: Optical Absorption of F_A-centre in alkali
halides.

The splitting of the excited state is
shown due to the overlap of the p-
like F-orbital with inequivalent im-
purity and host cations.
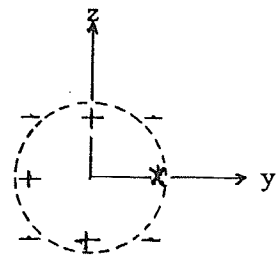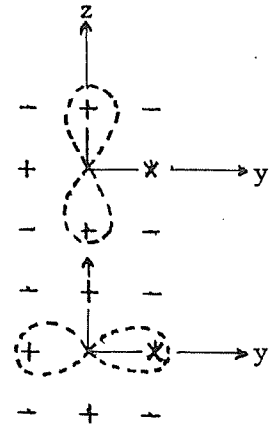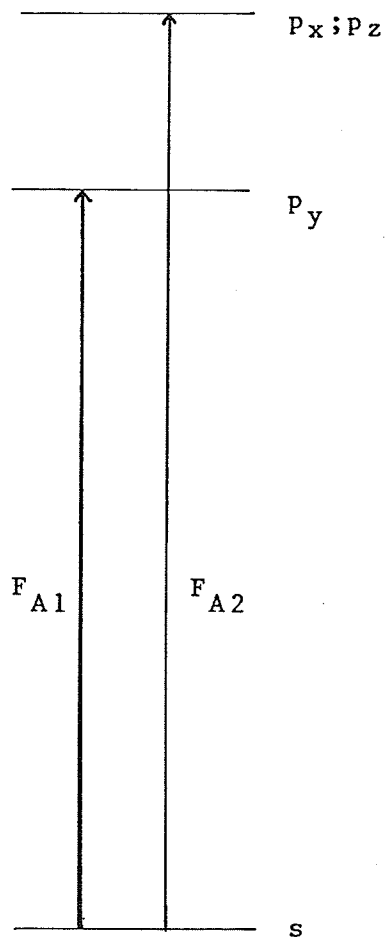
Before closing the discussion on pseudopotentials, it should be mentioned that there is another class of method, called the "model-pseudopotential", in close connection to the pseudopotential method. We have seen that the pseudopotential operator V_P is, in general, an angular-momentum, energy-dependent, integral operator (The BSG method suppresses the angular-momentum dependence by neglecting variation of ϕ_F over the core). This, although already a simplification, is still tedious to apply. The method of model-pseudopotential seeks to replace V_P by a multiplicative operator V_M defined as:

$$V_M(\vec{r}) = \sum_{\ell} V_{\ell}(E, \vec{r}) \hat{P}_{\ell} \qquad (1.30)$$

In (1.30), ℓ is the angular momentum quantum number, $\hat{P}_{\ell}$ is the projection operator which projects out the appropriate angular momentum component of ϕ_F onto the core manifold. V_{ℓ}'s are adjustable parameters. They are determined either by requiring the resultant eigenfunctions to best-fit the corresponding (atomic) Hartree-Fock eigenfunctions, or by requiring the resultant eigenvalues to best-fit the experimental atomic spectroscopic data. These are discussed by Evarestov[32]. A slightly different form of model potential has been derived and used by Woo and Wang[33]. Opik and Wood[14], whose work was discussed earlier under the extended-ion method, also made a similar assumption to (1.30) in treating the Coulomb and exchange interactions.

1.2.3 Statistical Exchange Method

A full Hartree-Fock self-consistent-field calculation on even a moderate-sized molecule is extremely difficult. One of the difficulties lies with the non-local nature of the exchange operator defined as:

$$X_i \, \phi_i \, (\vec{r}) \;=\; \left\{ \sum_j \int d\vec{r}' \; \phi_j^*(\vec{r}') \, \phi_i(\vec{r}') \, V_{ij} \right\} \phi_j(\vec{r}) \qquad (1.31)$$

where the summation is over all the occupied orbitals (core + defect) in the system, and V_{ij} is the interacting potential between electrons in orbitals ϕ_i and ϕ_j. Thus, the exchange operator X_i is different for all i. Slater suggested that the X_i's be replaced with a statistical average $\overline{X}_f$ over all the X_i's, and the respective orbitals ϕ_i's be replaced by free-electron orbitals (plane-waves) in calculating this average. This leads to a much simpler, local exchange potential given by[34]:

$$\overline{X}_f \;=\; -6 \left[\frac{3}{8\pi} \, \rho(\vec{r}) \right]^{1/3} \qquad (1.32)$$

where $\qquad \rho(\vec{r}) \;=\; \sum_j \phi_j^*(\vec{r}) \, \phi_j(\vec{r}) \qquad (1.33)$

The statistical exchange method has then been elaborated by Kohn and Shsm[69] and Gunnarsson, Lundquist and Wilkins[70], and has been widely used in calculating band structure in solids.

Chaney and Lin[35] and Chaney[36] have used this method to compute the electronic structure of the F-centre in LiF. Besides the free-electron exchange, this work differs from

the earlier ones in roughly two aspects. First, they used Gaussian orbitals rather than Slater's (Ong and Vail[26] and Leung and Song[16] have also used Gaussians). Second, instead of using free Hartree-Fock core orbitals, the orbitals they used are obtained from a previous band structure calculation of LiF perfect crystal. In addition to this, they also attempted to treat the polarization of the cores by iteration, but the iteration is done only once. Thus, the result is not self-consistent.

Another approach which makes extensive use of the free-electron exchange is the multiple-scattering X_α method proposed by Slater and Johnson[37]. The details of this method have been discussed thoroughly by Slater[38], and have been applied to colour centre problems by Yu, DeSiqueira and Connolly[39].

1.3 OBJECTIVES OF THE PRESENT WORK

Results of some of the calculations illustrative of the methods reported in the last section will be presented in Chapter 3. The general conclusions are as follows:

(a) While the extended-ion method showed some promise in defect calculations, its development in the past has been greatly limited by the amount of computation required. Consequently, many simplifying assumptions have been made (neglect of self-consistent core readjustment, evaluation of multicentre integrals, etc.), all of which tend to mask the actual strength of the method.

(b)   The BSG pseudopotential method[24], although showing improved results for the F-centre absorption energies, cannot be straightforwardly extended to treat other types of defects. This is evident from the results obtained in F_A-centres. In any case, the empirical factor of $\alpha = 0.53$ which is necessary in order to get agreement with experiments in F-centres, and which has to be readjusted when applied to other centres, is theoretically unpleasing.

Thus, to date, the treatment of ion-size effects in the physics of colour centre is inadequate. The present work is an attempt to rectify this. Recently, a new class of calculation, called the cluster calculation, has been very popular in the study of surface and catalysis properties, and has contributed much understanding to the field[40]. The extension of the cluster method to the study of localized phenomena in bulk solid has been discussed by Cartling[41]. Kunz and Klein[45] have proposed a particular cluster model appropriate for ionic solids and have pointed out the applicability of this model to colour centre porblems, the details of which will be described in the next chapter. The object of the present work is to make an assessment of the reliability of this cluster method by applying it to calculate the optical and magnetic properties of F and F_A-centres in a variety of alkali halides. It should be pointed out at the start that such an approach is still far from a complete treatment with sufficient generality to give quantitative

accuracy when applied to the whole class of point defects in ionic materials, since, in such a theory, amongst other things, lattice relaxation, electron-phonon interaction, and correlation effect, must be included, all of which have been neglected here. Rather, by focusing the effort on a specific aspect, namely the ion-size effect (of the first nearest neighbours), we hope to initiate an alternative viewpoint from which the problem is approached, and at the same time, to elucidate the importance of some features which were either neglected or approximated in previous work.

Chapter II

THE UNRESTRICTED HARTREE-FOCK (UHF) CLUSTER MODEL

We start quite generally by considering the crystal as an interacting many-body problem, which consists of a number of electrons and a more or less regular array of nuclei. Because of the vast difference between the electronic and nuclear masses, the Born-Oppenheimer approximation is invoked to "separate" the electronic from the nuclear motion. The resulting electronic Schroedinger equation then depends only parametrically on the set of nuclear co-ordinates $\underline{R}$, while its eigenvalue $E_e(\underline{R})$ forms the potential energy term of the nuclear equation. Since we are not going to be concerned with phonon effects, the nuclear equation will not be discussed any further, but it is through this assumption that we can treat the electronic problem with a static lattice.

Exact analytical solution of the quantum mechanical many-body problem, except in the simplest case of the hydrogen molecule, is unattainable. The Hartree-Fock self-consistent-field method is probably the most viable approximation to the exact solution available today. This is taken up in the following section.

2.1   HARTREE-FOCK SELF-CONSISTENT-FIELD (SCF) THEORY

Many excellent articles on the Hartree-Fock theory are available in the literature, notably the ones by Lowdin[42] and Slater[43]. A summary will be given below.

The Hamiltonian of a system of electrons with mutual Coulomb interaction in the presence of a static lattice of nuclei can be written as:

$$\mathcal{H} = T_e + V_{eN} + V_{ee} + V_{NN} \tag{2.1}$$

where T_e = electron kinetic energy operator

$$= \sum_{j=1}^{N} \frac{(-\nabla_j^2)}{2} \tag{2.2}$$

V_{eN} = electron-nuclear interaction

$$= \sum_{j=1}^{N} \sum_{\nu=1}^{M} \frac{-Z_\nu}{|\vec{r}_j - \vec{R}_\nu|} \tag{2.3}$$

N,M = number of electrons and nuclei respectively

Z_ν = charge of ν -th nucleus

$\vec{R}_\nu$ = position of ν -th nucleus

V_{ee} = electron-electron interaction

$$= \frac{1}{2} \sum_{jj'} \frac{1}{|\vec{r}_j - \vec{r}_{j'}|} \tag{2.4}$$

V_{NN} = nuclear-nuclear interaction

$$= \frac{1}{2} \sum_{\nu\nu'} \frac{Z_\nu Z_{\nu'}}{|\vec{R}_\nu - \vec{R}_{\nu'}|} \tag{2.5}$$

Unless otherwise stated, atomic units will be used throughout this work, in which $\hbar$ (Planck's constant divided by 2π), electronic charge e and electronic mass m are all

equal to unity. Energy is measured in unit of the Hartree (or atomic unit a.u.) and distance in Bohr radii a_0:

$$\hbar = e = m = 1$$

$$1 \text{ a.u. } = 2 \text{ Rydberg } = 27.21 \text{ eV.}$$

$$1 \text{ a}_0 = 0.529 \text{ A} = 0.529 \times 10^{-8} \text{ cm.}$$

The rigorous wavefunction of this N-body problem can be written as a linear combination of some complete set of basis states Φ_i:

$$\Psi = \sum_i C_i \Phi_i \qquad (2.6)$$

where each Φ_i is made up of a fully antisymmetrized product of N one-particle functions ϕ_j picked from a complete orthonormal set $\{ \phi_1(x_1) \cdots \phi_j(x_j) \cdots \}$ in Hilbert space. Equivalently, each Φ_i can be written in determinantal form called the Slater's determinant, referred to as a "configuration" of the system:

$$\Phi_i(x_1 \cdots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \cdots & \cdots & \phi_N(x_1) \\ \vdots & & & \vdots \\ \vdots & & & \vdots \\ \phi_1(x_N) & \cdots & \cdots & \phi_N(x_N) \end{vmatrix} \qquad (2.7)$$

The x_i's in (2.7) represent the space-spin co-ordinates (r_i, σ_i) of the one-particle function concerned. The requirement of antisymmetry is the consequence of Pauli's Principle. All the physics of the system is contained in the solution to the eigenvalue problem:

$$\mathcal{H}\Psi = E\Psi \qquad\qquad (2.8)$$

In principle, one can take a straightforward approach by choosing a complete set or almost complete set $\{\phi_i(x_i)\}$, construct all possible configurations $\bar{\Phi}_i$, set up (2.6) and substitute it into (2.8). Then, one ends up with an essentially infinite dimensional secular equation from which the set of eigenvalues E and expansion coefficient C_i's can be solved. However, it is immediately obvious that, except in the case of small molecules (small N) and when the expansion (2.6) can be truncated after a few configurations, such an approach has no practical importance.

The Hartree-Fock (HF) method approximates the system wavefunction with a single Slater determinant, with constituent one-particle functions ϕ_j's variationally chosen to minimize the total energy:

$$\frac{\delta}{\delta\phi_j}\left[<\Psi^{HF}\mid\mathcal{H}\mid\Psi^{HF}>\right] = 0$$

The variational procedures (see, for example, P.256 of Ref. 43) lead to a set of simultaneous integro-differential one-particle equations defining the ϕ_j's:

$$F \phi_i = \sum_j \phi_j \lambda_{ji} \tag{2.9}$$

where $\quad$ F = Fock operator = $-\dfrac{\nabla^2}{2} - \sum_\nu \dfrac{Z_\nu}{|\vec{r} - \vec{R}_\nu|}$

$$+ \int dx' \frac{\rho(x', x')}{|\vec{r} - \vec{r}'|}$$

$$- \int dx' \, \rho_F(x, x') |\vec{r} - \vec{r}'|^{-1} P(x, x') \tag{2.10}$$

$\rho_F(x, x')$ = Fock-Dirac density operator

$$= \sum_{j=1}^{N} \phi_j(x) \, \phi_j^\dagger(x') \tag{2.11}$$

$P(x, x')$ = operator which interchanges co-ordinates x and x'.

λ_{ji} in (2.9) are Lagrange multipliers to ensure normalization of the ϕ_j's. Note that $\int dx' \rho_F(x, x')$ as defined in (2.10) is an one-particle integral operator while $\rho(x', x')$ is simply the charge density:

$$\int dx' \, \rho_F(x, x') \, \phi_i(x') = \int dx' \sum_j \phi_j(x) \, \phi_j^\dagger(x') \, \phi_i(x') \tag{2.12}$$

$$\rho(x' x') = \sum_j \phi_j^\dagger(x') \, \phi_j(x')$$

Also, summation over spin variables is implicit within the integration

$$\int dx \equiv \sum_\sigma \int d^3r$$

The four terms appearing in the Fock operator F in (2.10) can be identified as the kinetic energy, nuclear attraction, Coulomb, and exchange operators respectively.

A very important consequence of the HF approximation is that the solution set { $\phi_j(x)$ } of (2.9) is not unique, but arbitrary to an unitary transformation amongst themselves. Thus, if { ϕ_j } is one solution set, so is { ϕ_j' } defined by:

$$\phi_j' = \sum_k U_{jk} \phi_k$$

where U_{jk} is the element of any unitary matrix U. This can be proved by considering that if U takes the HF wavefunction Ψ to Ψ' (the superscript "HF" will be dropped from now on and denote the matrix associated to the determinantal wavefunction Ψ by $\Psi_{(M)}$), then

$$\Psi' = Det \left| \Psi'_{(M)} \right| = Det \left| U \Psi_{(M)} \right|$$

$$= Det |U| \, Det \left| \Psi_{(M)} \right| = Det \left| \Psi_{(M)} \right| = \Psi$$

because Det $|U|$ = 1 for any U.

The qualitative implication is this: The variational solution of the Fock equations (2.9) leads to a N-dimensional manifold in Hilbert space spanned by { $\phi_1 \cdots \phi_N$ } that minimizes the total energy. But the specific representation of this manifold is immaterial as one is free to make any linear transformations which preserve normalization amongst the ϕ_i' s. In essence, the solutions to the Fock equation divide the Hilbert space into two subspaces, the Fock space spanned by the solution set and the space outside it. A function within the Fock space is called an occupied orbital while one which is not is called a virtual orbital. The ar-

bitrariness of Ψ will be exploited further in the next sec-
tion. The common representation to use is one in which the
λ -matrix in (2.9) is diagonal. When this is done, the text
book form of the Fock equation is retrieved:

$$F \phi_i = \epsilon_i \phi_i \tag{2.13}$$

The occupied ϕ_i's in this representation are then called
natural spin orbitals, the eigenvalue ϵ_i has the usual mean-
ing of ionization energy in the context of Koopmans' Theorem
and the optimum total energy is given by:

$$E^{HF} = \langle \Psi | \mathscr{H} | \Psi \rangle$$

$$= \sum_{i=1}^{N} \epsilon_i$$

$$+ \frac{1}{2} \sum_{ij} \left\{ \int dx_1 dx_2 \, \phi_i^*(x_1) \phi_j^*(x_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_i(x_1) \phi_j(x_2) \right.$$

$$\left. - \int dx_1 dx_2 \, \phi_i^*(x_1) \phi_j^*(x_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_j(x_1) \phi_i(x_2) \right\} \tag{2.14}$$

Even at the level of Hartree-Fock approximation, solu-
tions are very difficult to obtain. Since F is a function
of the ϕ_i's, a self-consistent iterative method of solution
is evidently required (and thus the name self-consistent-
field). Accordingly, successive constraints are placed on
the ϕ_i's to ease the effort required. They are listed be-
low:

(a)   Generalized Hartree-Fock (GHF): (2.13) is solved in
full generality with no assumptions made. Solution at this
level has not been attained.

(b)   Unrestricted   Hartree-Fock (UHF): Each orbital is re-
quired to be an eigenfunction of the spin operator S_z. Thus,
each one -particle function $\phi_i(x_i)$ takes the product from
$\phi_i(\vec{r}_i)\,\chi(\sigma)$ where $\chi(\sigma)$ is either the spin up eigenfunc-
tion $\alpha(\sigma)$ or spin down eigenfunction $\beta(\sigma)$.   There is no
restriction on the spatial function $\phi_i(\vec{r}_i)$.

(c)   Restricted Hartree-Fock (RHF): The spatial orbitals ϕ_i
are required to be doubly occupied (one for each spin) as
far   as   possible.   An N-electron system would then occupy
only N/2 spatial orbitals (N/2 + 1 if N is odd), with each
spin orbital pair having equivalent spatial part:

$$\phi_i(x_i) \;=\; \phi_i(\vec{r}_i) \begin{cases} \alpha(\sigma) \\[1em] \beta(\sigma) \end{cases} \qquad i = 1, \cdots \frac{N}{2}$$

Also, each ϕ_i is required to be a symmetry orbital which
transforms according to one of the irreducible representa-
tions of the point group of the crystal lattice.   It is this
level which is referred to as the Hartree-Fock approximation
in common text books.

There   have   been   numerous   <u>ab-initio</u>   Hartree-Fock   energy
band calculations in perfect crystals[44] during the past
ten years or so, largely because of the availability of
larger and faster computers.   For an imperfect solid, the
simplification due to perfect translational symmetry in the
band model cannot be carried over.   In this case, the clus-
ter model, which had been applied successfully to surface
and catalysis[40] studies, will be more appropriate.

2.2 CLUSTER MODEL

In the cluster model, a spatially finite subsystem is singled out for intensive study, while the presence of the rest of the system, called the environment of the cluster, is simulated by some appropriate boundary condition imposed on the solution of the cluster equations. Two questions immediately arise. First, how should the partition between the cluster and the environment be done? Second, what kind of boundary condition is appropriate?

The answers to these questions, of course, depend on the nature of the system, and the particular properties which are under investigation. Thus, in the case of a perfect crystal, the natural cluster-environment partition would be the unit cell. In the case of a defect crystal, the size of the cluster must be sufficiently large so that the range of the perturbation due to the presence of the defect is covered. For this reason, only localized phenomena are suitable for cluster study and even then, some trade-off between computational simplicity and theoretical rigor is inevitable.

The question of boundary condition in ionic solids had been studied recently by Kunz and Klein[45], based on the theory of localized orbital developed by Adams[46], and further elaborated by Gilbert[47] and by Kunz[48]. Since this boundary condition will be used in the present work, it is reviewed in some detail below.

The localized orbital theory further exploits the arbitrariness inherent in the HF determinantal wavefunctions. With reference to what has been said in the previous section, we note that the Fock-Dirac density operator as defined by (2.11) and (2.12) is actually a projection operator onto a particular manifold of Fock space, property:

$$\rho_F \, \phi = \phi \qquad \text{if } \phi \text{ is an occupied orbital}$$

$$\tag{2.15}$$

$$\rho_F \, \phi' = 0 \qquad \text{if } \phi' \text{ is an virtual orbital}$$

If A is an arbitrary one-electron operator, it is possible to form the projection of A onto the HF manifold as

$$A^{(F)} = \rho_F A \rho_F \tag{2.16}$$

with the consequence

$$A^{(F)} \phi_i = \sum_{j=1}^{N} \phi_j \, \gamma_{ji} \tag{2.17}$$
$$A^{(F)} \phi_i' = 0$$

since $\{ \phi_1 \cdots\cdots \phi_N \}$ span the HF manifold. (2.17) has the same form as the general Fock equation (2.9). By adding (2.17) to (2.9), we get

$$\left[F + A^{(F)} \right] \phi_i = \sum_{j=1}^{N} \phi_j \left(\lambda_{ji} + \gamma_{ji} \right) \tag{2.18}$$

which is again structurally identical to the general Fock equation. Thus, a unitary transformation may be sought to diagonalize the matrix $(\underline{\underline{\lambda}} + \underline{\underline{\gamma}})$ to yield:

$$\left[F + A^{(F)} \right] \phi_i = \pi_i \, \phi_i \tag{2.19}$$

(2.19) is called the modified HF equation. Gilbert[47] has shown rigorously that orbitals localized on individual nuclei can be obtained by choosing A variationally, and A is called the localizing potential in this context.

Suppose, for the system under study, that the partition into the cluster C and environment E is made. It is obviously impossible to localize all the N electrons of the entire system within C, and a number of electrons, say N_C, has to be assigned to it. For ionic systems, at least, there should be no ambiguity as to the appropriate value of N_C. The Fock operator, F, can then be written as:

$$F = F_C + U_C$$

where F_C is the part of F which includes kinetic energy, nuclear attraction, electron-electron Coulomb and exchange potentials of the N_C electrons within C while U_C is the rest of F which includes the interaction of C with E, and E itself. The modified HF equation becomes:

$$\left[F_C + U_C + \rho_F A \rho_F \right] \phi_i = \pi_i \phi_i \qquad (2.20)$$

For ionic systems, the environmental potential U_C can further be divided into two parts, a long-range part V_C^M which is the Madelung potential and a short-range part V_C^S which is the rest of U_C. Now, if one chooses $A = -V_C^S$ and makes use of the projection operator property of ρ_F, i.e., $\rho_F \phi_i = \phi_i$, equation (2.20) becomes

$$\left[F_C + V_C^M \right] \phi_i = \pi_i \phi_i - V_C^S \phi_i + \rho_F V_C^S \phi_i \qquad (2.21)$$

For ionic systems, the N_C orbitals localized in C should only weakly penetrate E and V_C^S should only weakly penetrate C. Thus, when self-consistency is acheived, the last two terms of (2.21) cancel, and the appropriate equation including cluster-environment interaction reduces to

$$\left[F_C + V_C^M \right] \phi_i = \pi_i \phi_i \qquad (2.22)$$

Equation (2.22) implies that the suitable boundary condition to use in a cluster calculation in ionic systems is the long-range Madelung Potential of the ions in the environment. The total energy expression can be derived in a similar way. We split the Hamiltonian $\mathcal{H}$ into a cluster part $\mathcal{H}_C$, an environment part $\mathcal{H}_E$ and an interaction part $\mathcal{H}_{CE}$:

$$\mathcal{H} = \mathcal{H}_C + \mathcal{H}_E + \mathcal{H}_{CE} \qquad (2.23)$$

where

$$\mathcal{H}_C = -\sum_{i \in C} \frac{\nabla_i^2}{2} - \sum_{i \in C} \sum_{\nu \in C} \frac{Z_\nu}{|\vec{r_i} - \vec{R_\nu}|}$$
$$+ \frac{1}{2} \sum_{i \in C} \sum_{j \in C} \frac{1}{|\vec{r_i} - \vec{r_j}|} \qquad (2.24)$$

$$\mathcal{H}_{CE} = \sum_{i \in C} \sum_{\nu \in E} \frac{-Z_\nu}{|\vec{r_i} - \vec{R_\nu}|} + \sum_{i \in E} \sum_{\nu \in C} \frac{-Z_\nu}{|\vec{r_i} - \vec{R_\nu}|}$$
$$+ \sum_{i \in C} \sum_{j \in E} \frac{1}{|\vec{r_i} - \vec{r_j}|} \qquad (2.25)$$

and a similar expression to (2.24) for $\mathcal{H}_E$, with E replacing C in the summation. The energy corresponding to (2.23) can also be denoted by

$$E = E_C + E_E + E_{CE} \qquad (2.26)$$

Since ultimately, we are going to be concerned with energy differences only, and if a Koopmans'-like approximation is made on E, i.e., the orbitals in E is frozen as those in C undergo excitation, (this is reasonable if the excitation is localized in nature, or alternatively, the size of the cluster is large enough), then, E_E is constant and can be dropped from (2.26). The interaction term H_{CE}, however, is still unmanageable and further approximation has to be made. Writing out the interaction energy explicitly:

$$E_{CE} = \sum_{i \in C} \langle \phi_i | \sum_{\nu \in E} \frac{-Z_\nu}{|\vec{r}_i - \vec{R}_\nu|} | \phi_i \rangle + \sum_{i \in E} \langle \phi_i | \sum_{\nu \in C} \frac{-Z_\nu}{|\vec{r}_i - \vec{R}_\nu|} | \phi_i \rangle$$

$$+ \sum_{i \in C} \sum_{j \in E} \left\{ \langle \phi_i \phi_j | \frac{1}{|\vec{r}_i - \vec{r}_j|} | \phi_i \phi_j \rangle \right.$$

$$\left. - \langle \phi_i \phi_j | \frac{1}{|\vec{r}_i - \vec{r}_j|} | \phi_j \phi_i \rangle \right\} + \sum_{\nu \in C} \sum_{\mu \in E} \frac{Z_\nu Z_\mu}{|\vec{R}_\nu - \vec{R}_\mu|} \quad (2.27)$$

The last term of (2.27) is a nuclear-nuclear interaction term brought in from the static lattice energy, equation (2.5). We proceed to simplify the expression for E_{CE} by resorting to the weak interpenetrations amongst the orbitals in C and E. In the limit of spherically symmetric atomic charge distribution and no overlap between C and E, (2.27)

reduces to a very simple form:

$$E_{CE} \longrightarrow E_{CE}^{(0)} = \sum_{\nu \in C} \sum_{\mu \in E} \left\{ \frac{-N_\nu Z_\mu}{|\vec{R}_\nu - \vec{R}_\mu|} + \frac{-N_\nu Z_\nu}{|\vec{R}_\nu - \vec{R}_\mu|} \right.$$

$$\left. + \frac{N_\nu N_\mu}{|\vec{R}_\nu - \vec{R}_\mu|} + \frac{Z_\nu Z_\mu}{|\vec{R}_\nu - \vec{R}_\mu|} \right\} \tag{2.28}$$

Where N_ν is the number of electrons associated with the ν-th nucleus. Defining the ionicity of the ν-th nucleus I_ν as

$$I_\nu = N_\nu - Z_\nu \tag{2.29}$$

(2.28) finally takes the form:

$$E_{CE}^{(0)} = \sum_{\nu \in C} \sum_{\mu \in E} \frac{I_\nu I_\mu}{|\vec{R}_\nu - \vec{R}_\mu|} \tag{2.30}$$

Thus, in the zeroth-order approximation, the total energy of the system reduces to the energy of the cluster plus the Madelung contribution from the environment on the cluster. In reality, there certainly is some overlap between the cluster and the environment. Further, the zeroth order approximation is clearly not sufficient for optical excitation problems, since, unless lattice distortion is considered explicitly in the initial and final states of the transition, $E_{CE}{}^{(0)}$ is a constant. In the first order approximation, the penetration of the orbitals of C into E (but not vice versa) is retained, and the exchange effect is ignored. According

to (2.27), this leads to

$$E_{CE} \longrightarrow E_{CE}^{(1)} = \sum_{i \in C} \langle \phi_i | \sum_{\nu \in E} \frac{-Z_\nu}{|\vec{r}_i - \vec{R}_\nu|} | \phi_i \rangle$$

$$+ \sum_{\mu \in E} \sum_{\nu \in C} \frac{-N_\mu Z_\nu}{|\vec{R}_\mu - \vec{R}_\nu|}$$

$$+ \sum_{i \in C} \langle \phi_i | \sum_{\nu \in E} \frac{N_\nu}{|\vec{r}_i - \vec{R}_\nu|} | \phi_i \rangle$$

$$+ \sum_{\nu \in C} \sum_{\mu \in E} \frac{Z_\nu Z_\mu}{|\vec{R}_\mu - \vec{R}_\nu|}$$

Using (2.29),

$$E_{CE}^{(1)} = \sum_{i \in C} \langle \phi_i | \sum_{\nu \in E} \frac{I_\nu}{|\vec{r}_i - \vec{R}_\nu|} | \phi_i \rangle$$

$$+ \sum_{\nu \in C} \sum_{\mu \in E} \frac{-I_\mu Z_\nu}{|\vec{R}_\mu - \vec{R}_\nu|} \qquad (2.31)$$

In this approximation, the interactions of the cluster orbitals with the point-ion potential of the environmental ions are included.

2.3 UHF-CLUSTER MODEL APPLIED TO COLOUR CENTRE PROBLEMS

The ground states of the F or F-like centres in alkali halides are localized defects and therefore are well-suited to be studied with the cluster model using the above boundary conditions. This possibility was originally pointed out by Kunz and Klein[45], although, in their paper, they have chosen the perfect LiF crystal to illustrate the method. In the present work, a systematic study of the optical and

ground state magnetic properties of F and F_A-centres in a series of alkali halides has been carried out, using the UHF-cluster model. The cluster is taken to consist of the F-electron and its six nearest neighbouring ions, while the rest of the crystal (the environment) becomes point charges representing the long-range part of the Coulomb field. This is illustrated in fig.3. Up to 18 shells of ions are included in the environment E, and to give the correct Madelung potential, the ions situated on faces and corners of E are given fractional charges according to the Evjen scheme[71], to maintain the overall electrical neutrality of the system.

The cluster Fock equation (2.22) is then solved self-consistently. No further approximations are made, theoretically or numerically, other than those inherent in the UHF method and cluster model. Despite the fact that a UHF calculation is computationally much more complex to carry out than a RHF, its superiority in cluster calculations is considerable. This had been discussed by Marshall, Blint and Kunz[48]. In the context of F-centre problems, the UHF method should be used for at least two reasons:

(a)   The exchange term (the last term in (2.10)) in the HF equation can be written as:

$$V_x \, \phi_i(x_i) \;=\; \sum_j \phi_j(x_i) \int dx_j \frac{\phi_j(x_j)\,\phi_i(x_j)}{|\vec{r}_i - \vec{r}_j|} \qquad (2.31)$$

Fig. 3 : Cluster Model for F-Centre in Alkali Halides.
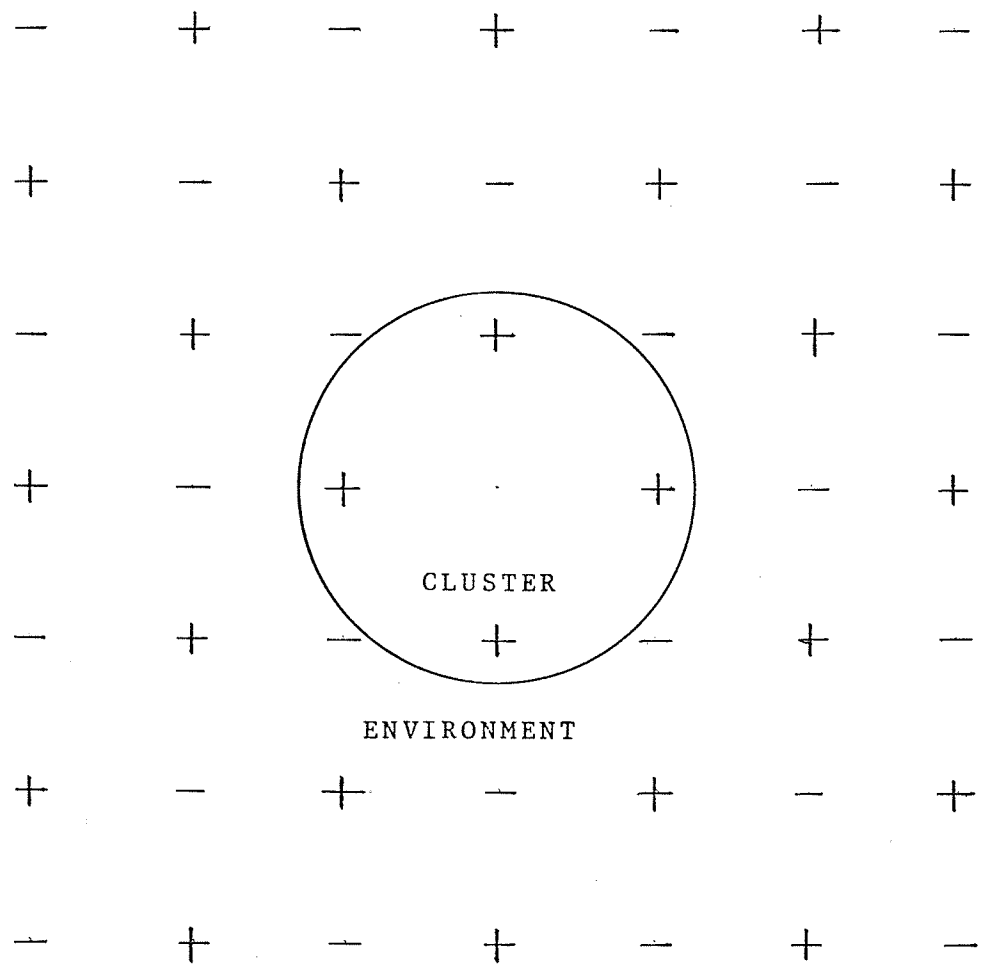
Because the integration over dx_j involves summation over spin variables, the terms in the summation in (2.31) will vanish <u>unless</u> ϕ_j and ϕ_i in the integrand have parallel spin. The F-electron is an unpaired electron while the rest of the ions have closed-shell structures. The consequence is that the spin "up" orbitals should see a different exchange potential than their spin "down" counterparts. This effect is called "spin-polarization". The RHF method has completely ignored this by forcing the spin up and spin down orbital-pairs to have identical spatial parts. This may impose undue constraint on the energetics of the system.

(b) In a RHF calculation, because of the exact cancellations between equivalent spin up - spin down orbital pairs, the only contribution to the spin density is from the orbital representing the F-electron (and its overlaps with the neighbours). By relaxing this constraint, the cancellation will not be exact and each orbital may contribute to the net spin density. There has been wide speculations on the importance of spin polarization effects in previous colour centre calculations. A UHF calculation may elucidate this point.

According to the above account, it is clear that the UHF approach is, at least in principle, more appropriate in paramagnetic centres. On the other hand, for non-paramagnetic centres (for example, a U-centre consisting of a negative hydrogen ion trapped in an anion vacancy), the RHF result is

expected to be the same as the UHF's and one need not go through the extra computational tedium (one need not eigen-analyse the Fock matrix twice, once for each spin, per iteration).

The optical absorption energies, ground state isotropic and the axially symmetric anisotropic hyperfine constants of F and F_A-centres in a series of alkali halides have been calculated, using the UHF-cluster model. The results are reported in the next chapter. This, we believe, will constitute a fairly complete assessment of the applicability of our model to the ion-size effect in defect calculations.

Chapter III

CALCULATIONS AND RESULTS

3.1   METHOD OF COMPUTATION

The equation to be solved is the Hartree-Fock equation for a molecular cluster consisting of the F-centre and its six nearest neighbours embedded in the crystal Madelung potential.   The Roothaan expansion method[50] in terms of gaussian type orbitals (GTO) is used.   Each one-electron molecular orbital (MO) is expressed as a linear combination of atomic orbitals (LACO) localized on the various nuclear sites.   The atomic orbitals are in the form of Cartesian gaussians χ.   Thus a molecular orbital ϕ_i is:

$$\phi_i = \sum_\nu \sum_{j=1}^{M_\nu} c_{\nu j}^{(i)} \chi_{\nu j}(\alpha_{\nu j}; \ell_j, m_j, n_j; \vec{r}_\nu) \qquad (3.1)$$

where

$$\chi_{\nu j} = N_j \, x_\nu^{\ell_j} \, y_\nu^{m_j} \, z_\nu^{n_j} \, e^{-\alpha_{\nu j} r_\nu^2} \qquad (3.2)$$

N_j is the normalization constant, x_ν, y_ν, z_ν and r_ν are coordinates measured with respect to the ν-th nuclear site, ℓ_j, m_j and n_j are indices giving the angular dependence of χ (Thus, $1_j = m_j = n_j = 0$ corresponds to a s-function, $1_j = m_j = 0$, $n_j = 1$ corresponds to to a p_z-function, etc.), M_ν is the number of atomic orbitals (AO) to be localized on site

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ν. $\alpha_{\nu j}$ is a set of chosen exponents spanning a suffi-
ciently wide range to give maximum flexibility in the varia-
tional calculation, and $C_{\nu j}^{(i)}$ are sets of variational parame-
ters determined by minimizing the total energy.

In general, the minimization problem with expansion (3.1)
leads to the secular equation:

$$\text{Det} \mid F_{ij}^{(AO)} - E\, S_{ij} \mid = 0 \qquad\qquad (3.3)$$

where $F_{ij}^{(AO)}$ is the Fock matrix element over the AO basis
(the $\chi_{\nu j}$'s), and S_{ij} are the elements of the overlap ma-
trix. The eigenvalues and eigenvectors are solved and the
process repeated many times until self-consistency is
acheived. In practice, an eigenvalue probelm with a non-or-
thogonal basis is difficult to solve, and the AO basis is
transformed to an orthonormal molecular orbital (MO) basis
before the eigen-analysis. The Algorithm for the SCF calcu-
lation is summarized below:

(i)   The set of AO is read in and the Fock matrix $F^{(AO)}$
over the AO basis is formed.

(ii)   A Transformation matrix $\underline{\underline{T}}^{(initial)}$ which is the ini-
tial guess to the solution eigenvectors is read in. The ov-
erlap matrix $\underline{\underline{S}}$ is formed:

$$S_{ij} = \langle \phi_i^{(I)} \mid \phi_j^{(I)} \rangle$$

where $\quad \phi_i^{(I)} = \sum_j T_{ij}^{(initial)} \chi_j$

(iii)   A new Transformation matrix $\underline{\underline{T}}^{(0)}$ is constructed to give an orthonormal MO basis set by diagonalizing S:

$$\underline{\underline{T}}^{(0)\dagger} \; \underline{\underline{S}} \; \underline{\underline{T}}^{(0)} = \underline{\underline{1}}$$

(iv)   The Fock matrix is transformed to the new MO basis.

$$\underline{\underline{F}}^{(0)} = \underline{\underline{T}}^{(0)\dagger} \; \underline{\underline{F}}^{(AO)} \; \underline{\underline{T}}^{(0)}$$

(v) $\underline{\underline{F}}^{(0)}$ is diagonalized to give eigenvalues and eigenvectors $\underline{\underline{C}}^{(0)}$ over the MO basis.

(vi)   A new transformation matrix $\underline{\underline{T}}^{(1)}$ is obtained by back transformation:

$$\underline{\underline{T}}^{(1)} = \underline{\underline{C}}^{(0)} \; \underline{\underline{T}}^{(0)}$$

(vii)   Go back to (iv) to form $\underline{\underline{F}}^{(1)}$ and iterate until convergence is acheived.

Notice that at convergence, $\underline{\underline{C}}^{(n)} = \underline{\underline{1}}$ and the self-consistent eigenvectors are contained in $\underline{\underline{T}}^{(n)}$. Thus, after each iteration, the deviation of $\underline{\underline{C}}^{(n)}$ from a unit matrix is checked and when it falls under a certain specified convergence criterion, the program stops.

There is a growing preference towards GTO over the Slater-type orbital (STO) in recent work in molecular Physics because integrals involving GTO can be obtained in analytical form, and very efficient computer programs are available to handle this. The drawback is that many more of them have to be used in order to acheive the same level of accuracy as, say, the Double-Zeta Slater basis[25]. The increase in the number of basis functions corresponds to an increase in the dimension of the Fock matrix, which leads to

a considerable increase in computation time during the iterative solution. A common practice to get around this somewhat is to use contracted gaussian type orbitals (CGTO). Thus, instead of writing each AO as a single gaussian as in (3.2), one uses a linear combination of a few gaussians (usually two or three) with pre-determined coefficients instead:

$$\chi'_{\nu j} = \sum_{i=1}^{n_c} k_i \, \chi_{\nu j, i} \tag{3.4}$$

where n_c is the number of gaussians contracted to a single AO, k_i is the contraction coefficient and $\chi_{\nu j, i}$ is the Cartesian gaussian as given in (3.2). Since there is one variational coefficient attached to each AO, for the same number of gaussians, the use of CGTO has, in effect, reduced the dimension of the Fock matrix and the number of variational parameters. Provided that the contraction coefficients k_i are carefully chosen, the CGTO are capable of giving results of comparable accuracy to their uncontracted counterparts[51]. These coefficients, for a wide variety of atoms and ions, have been computed and tabulated in the literature[52], and are used in most of the calculations in the present work.

The integrals necessary for the calculations are evaluated using the Caltech version of the POLYATOM integral program while the SCF calculations are done with programs based on the UHFONE program written by Surratt in the University

of Illinois at Urbana-Champaign. We are grateful to Prof.A.B. Kunz for making available to us these programs. The results of the various calculations are presented below.

3.2 RESULTS OF CALCULATIONS ON F-CENTRES

3.2.1 Optical Absorption energies

The F-electron undergoes optical excitation from an s-like state to a p-like state, giving rise to the distinct F-absorption band. Many experimental data on the absorption process are available and the absorption energy constitutes a first test for any theoretical model. Since the accuracy of a variational calculation depends on the flexibility of the trial wavefunction, it is desirable to test out the adequacy of the basis set employed here. Accordingly, calculations on the ground state of the F-centre in LiF are carried out for four different basis sets describing the nearest neighbour Li^+ ions:

(a)   11 s-functions, contracted to 4 s-type AO, denoted by (11s/4s) CGTO taken from Ref. 52.

(b)   (11s 1p/4s 1p), the s-functions are identical to those of (a) while the p-function has exponent $\alpha = 0.95$.

(c)   (11s 2p/4s 2p), same as (b) with an additional p-function of $\alpha = 0.20$.

(d)   (9s) uncontracted GTO formed from the original (7s) basis set used by Chaney and Lin in Ref.35 plus two additional s-functions with α's equal to 2.50 and 0.05 for extra flexibility.

In addition to the Li^+-centred functions mentioned above, there are four vacancy-centred s-functions in sets (a) to (c) and six in set (d) to describe the F-electron. Details of sets (a) and (d) are listed in Tables 1 and 2 respectively. Set (a) is primarily the basis set we want to use. Sets (b) and (c) assess the importance of "polarization functions" commonly used in quantum chemical calculations. The idea is to include higher angular momentum functions to account for the deviation from symmetry of the charge density from the atomic case when they combine to form a molecule. Note that each p polarization function actually corresponds to three addition functions in the set -- the p_x, p_y and p_z components. Set (d) includes within it as a subset the (7s)-basis set published by Chaney and Lin[35]. These authors had used this set in their calculations on the same subject, as referred to under section 1.2.3 of Chapter 1.

The ground state energy and the spin density at the N.N. Li^+ site are calculated using these four basis sets in turn. The results of the calculations are shown in Table 3. With reference to this table, two features are outstanding. Firstly, set (d), which is optimum in Chaney and Lin's calculation, yields the highest energy (0.46 eV. higher than (a) and 0.58 eV. higher than (c)). This is not particularly surprising, in retrospect, since the approach of Chaney and Lin is quite different from the present one, and what was

Table 1

Basis set (a) used in calculations on the
Ground state of F-centre in LiF.
(11s) contracted to (4s) by (3,3,2,3) is
used for the Li^+. Four vacancy-centred s-
functions are used for the F-electron. The
exponents are given in atomic units.

CENTRE	SYMMETRY	EXPONENTS	CONTRACTION COEFFICIENTS
Li^+	s	3184.467	0.0216
Li^+	s	480.512	0.1665
Li^+	s	108.863	0.8723
Li^+	s	30.289	0.1001
Li^+	s	9.641	0.3090
Li^+	s	3.339	0.6666
Li^+	s	1.249	0.7176
Li^+	s	0.467	0.3183
Li^+	s	0.079	−0.0547
Li^+	s	0.066	0.6988
Li^+	s	0.025	0.3937
vacancy	s	2.000	---
vacancy	s	0.750	---
vacancy	s	0.080	---
vacancy	s	0.015	---

Table 2

Basis set (d) used in calculations on ground
state of F-centre in LiF.
Uncontracted (9s) on Li^+ plus five s-functions on vacancy. Those marked with "*" are
added functions to the original set used in
Ref.35.

CENTRE	SYMMETRY	EXPONENTS
Li^+	s	921.27
Li^+	s	138.73
Li^+	s	31.94
Li^+	s	9.35
*Li^+	s	3.16
Li^+	s	2.50
Li^+	s	1.16
*Li^+	s	0.44
Li^+	s	0.05
vacancy	s	12.22
*vacancy	s	4.37
vacancy	s	2.50
*vacancy	s	0.36
vacancy	s	0.05

"optimum" in their case may not have the same validity here. Secondly, the polarization functions introduced in (b) and (c) do not give substantial improvement over (a) which contains s-functions only. Thus, with one polarization function as in (b), the energy is 0.07 eV. lower than (a), with two, as in (c), the energy is further lowered by 0.05 eV. The corresponding spin density is lowered by about 10%. However, with the inclusion of two polarization functions, the computation required is greatly increased as the number of basis functions is raised from 28 to 64. In view of the very mild improvement, we conclude that the CGTO set (a) is adequate for the purpose of the present calculation.

The ground states of the F-centre in lithium halides and potassium halides have now been calculated. The basis set used for the potassium ion is the (14s 10p/4s 3p) CGTO set taken also from Huzinaga[52], and is listed in Table 4. To get the energies of the first excited state, we have <u>not</u> made use of the virtual orbital energies obtained in the ground state, or invoked any frozen core approximation, since there may be fairly substantial readjustment of the electronic structure of the neighbouring ions as the F-electron undergoes excitation from an s-like to a p-like state. Instead, the entire calculation is repeated, with p_z-orbitals replacing the original s-orbitals centred on the vacancy. The absorption energies are then taken to be the dif-

Table 3

Results of claculations using the four basis
sets reported in text on ground state of F-
centre in LiF.

Basis set	Ground state energy (a.u.)	Spin Density at Li^+ (a.u.)
(a)	-52.6600	0.039
(b)	-52.6629	0.036
(c)	-52.6642	0.035
(d)	-52.6428	0.041

ference in the total energies of the two respective calculations. Lattice distortion is ignored throughout. Results are listed in Table 5[72], together with the results of some of the previous theoretical methods and experimental data for the sake of comparison. It has been known for a long time that the experimental absorption energies of F-centres in the sixteen NaCl-structured alkali halides are fairly well described by the empirical Ivey-Mollwo[53] relationship:

$$E_F = 62.7 \; a^{-1.84} \qquad (3.5)$$

where E_F is the absorption energy in eV. and a is the N.N. distance in Bohr radii. Fig. 4 is a plot of the UHF cluster results relative to the Ivey-Mollwo line. This gives a systematic display of deviation from experimental data.

3.2.2 Ground State Hyperfine Interactions

The F-electron is an unpaired electron which shows Zeeman splitting under an applied static magnetic field. It also interacts with the magnetic moment of the nuclei of the neighbouring ions to produce further splittings. The latter phenomenon is referred to as hyperfine interaction. The theory of hyperfine interactions in colour centres has been reviewed by Seidel and Wolf[9]. Neglecting quadrupole effects, the spin Hamiltonian is written as:

$$\mathcal{H}_{hf} = \frac{g_e \mu_B}{\hbar} \vec{B}_0 \cdot \vec{S} - \sum_\nu \frac{g_n \mu_N}{\hbar} \vec{B}_0 \cdot \vec{I}_\nu + \sum_\nu \vec{I}_\nu \cdot \underline{\underline{A}} \cdot \vec{S} \qquad (3.6)$$

<u>Table 4</u>

Basis set used in calculations of F-centre
in potassium halides.
(11s 10p) GTO contracted to (4s 3p) by
(4,4,3,3,4,3,3). Exponents are in atomic
units.

CENTRE	SYMMETRY	EXPONENTS	CONTRACTION COEFFICIENTS
K^+	s	78611.598	0.00627
K^+	s	12993.543	0.04102
K^+	s	3198.343	0.19859
K^+	s	910.206	0.82152
K^+	s	287.988	0.21254
K^+	s	102.797	0.41473
K^+	s	40.139	0.39113
K^+	s	15.598	0.08912
K^+	s	53.412	-0.08499
K^+	s	6.389	0.63027
K^+	s	2.427	0.44267
K^+	s	3.620	-0.16133
K^+	s	0.590	0.67613
K^+	s	0.210	0.44084
K^+	px;py;pz	1129.850	0.00504
K^+	px;py;pz	205.969	0.05471
K^+	px;py;pz	62.101	0.26499
K^+	px;py;pz	22.921	0.76368
K^+	px;py;pz	9.262	0.51882
K^+	px;py;pz	3.863	0.46252
K^+	px;py;pz	1.578	0.10747

K^+	px;py;pz	1.711	0.17659	
K^+	px;py;pz	0.570	0.58123	
K^+	px;py;pz	0.174	0.39087	
vacancy	s	2.000	---	
vacancy	s	0.750	---	
vacancy	s	0.080	---	
vacancy	s	0.015	---	

Table 5

Optical absorption energies of F-centre in
alkali halides. The numbers in brackets are
the corresponding lattice parameters in
units of Bohr radii taken from Tosi[68]. GA
is the point-ion calculation of Gourary and
Adrian taken from Ref. 7. WJ is the extend-
ed-ion calculations of Wood and Joy in
Ref. 13. BSG is the pseudopotential calcu-
lation due to Bartram, Stoneham and Gash
from Ref. 24. UHF is the results of the
present calculation. All energies are in
units of eV.

	GA	WJ	BSG	UHF	Experiment
LiF (3.807)	3.99	3.26	5.49	3.54	5.10
LiCl (4.858)	2.76	3.22	3.34	3.32	3.30
LiBr (5.200)	2.58	2.93	2.86	3.05	2.70
LiI (5.671)	2.14	--	2.48	2.65	3.27
KF (5.055)	2.60	2.81	2.93	3.02	2.85
KCl (5.949)	1.99	2.39	2.18	2.35	2.31
KBr (6.234)	1.83	2.26	1.98	2.22	2.06
KI (6.679)	1.64	--	1.80	2.03	1.88

where $\vec{B}_0$ is the applied field, g_e and g_N are the electron and nuclear g-factor respectively, $\mu_B = e\hbar/2mc$ is the Bohr magneton, $\mu_N = e\hbar/2m_p c$ is the nuclear magneton (m_p is the proton mass), $\vec{S}$ and $\vec{I}$ are the electron and nuclear magnetic moment operators, and $\underline{\underline{A}}$ is the (second rank) hyperfine interaction tensor. The summation is over all the nuclei in the system. The first term in (3.6) represents the electron Zeeman effect, the second is the nuclear Zeeman term and the third term, the hyperfine structure (hfs) term, represents the interaction between the electron and nuclear moments. Since only the nearest neighbours are included in the cluster in the present calculation, the summation and the subscript "ν" will be dropped in the subsequent discussion.

$\underline{\underline{A}}$ can be decomposed into an isotropic part "a" and an anisotropic part $\underline{\underline{B}}$. Following Slichter[54], the elements of a and B can be written as:

$$a(R_\mu) = \frac{8\pi}{3\hbar} g_e \mu_B g_N \mu_N S(R_\mu) \tag{3.7}$$

$$(B_\mu)_{ij} = \frac{g_e \mu_B g_N \mu_N}{\hbar} \int \left[\frac{3}{r_\mu^5} (r_\mu)_i (r_\mu)_j - \frac{1}{r_\mu^3} \delta_{ij} \right] S(\vec{r}_\mu) \, d\vec{r}_\mu \tag{3.8}$$

where $\vec{r}_\mu$ is the distance measured relative to the μ-th nucleus and $S(r)$ is the spin density at point $\vec{r}$. In the principal axes system (the representation in which $\underline{\underline{A}}$ is diagonal), $\underline{\underline{B}}$ can further be divided into an axially symmetric part b and one which measures the deviation from axial symmetry b$'$, defined as:

Fig. 4

Ivey-Mollwo plot of F-centre absorption energies.

The straight line is the theoretical Ivey-Mollwo relationship $E_F = 62.7 \, a^{-1.84}$.

The symbols are the results of the UHF cluster calculation. Energies are in units of eV. and distance in units of Bohr radii.

◇ : potassium halides

□ : lithium halide

IVEY-MØLLWØ PLOT
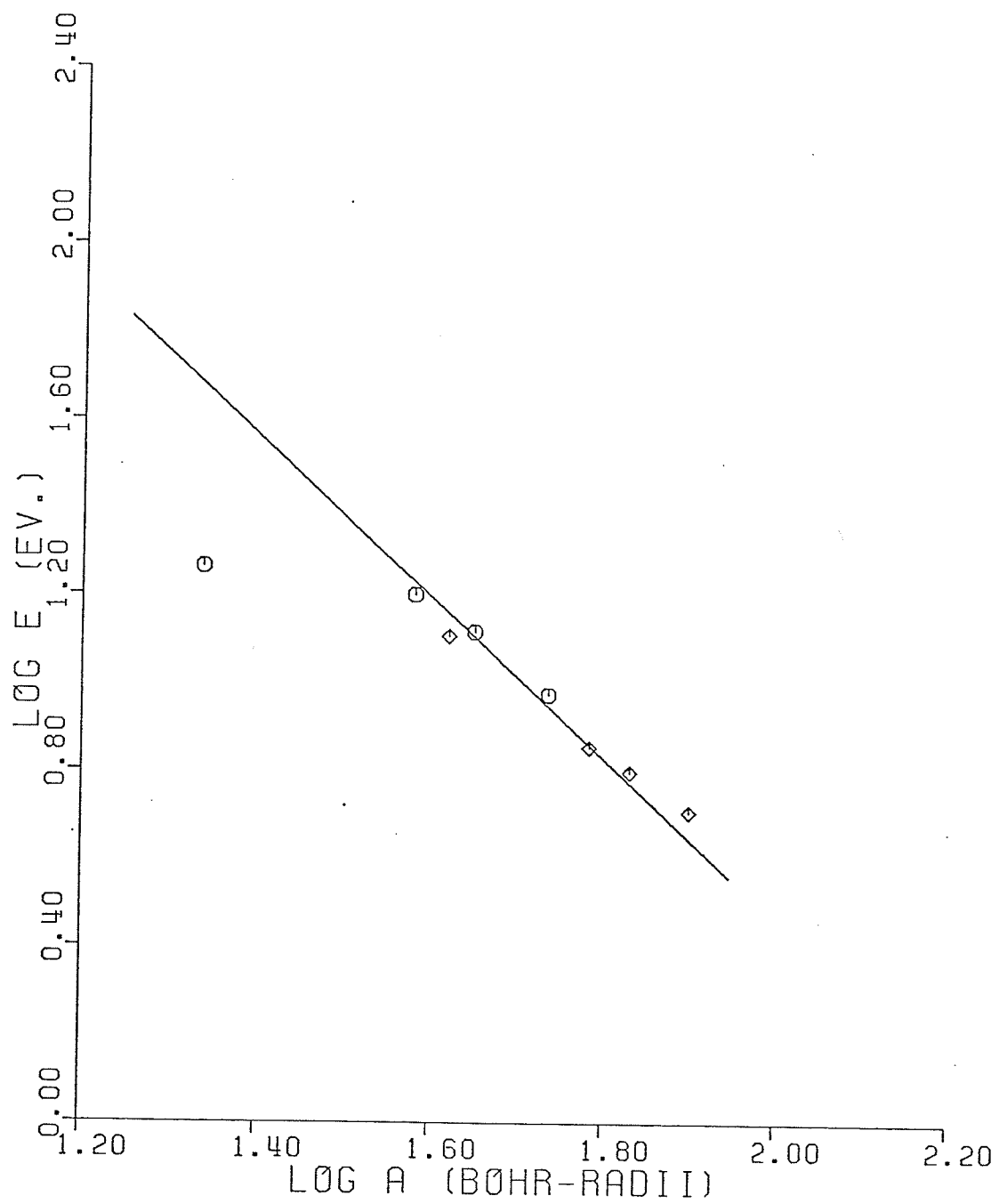
$$b = 1/2 \ B_{zz}, \tag{3.9}$$

$$b' = 1/2 \ (B_{xx} - B_{yy}). \tag{3.10}$$

For the nearest neighbours of an F-centre, $b\mu$ is zero while b_μ is given as[54]:

$$b_\mu = \frac{g e \mu_B g_N \mu_N}{2 \hbar} \int \left[\frac{3 \, \partial_\mu^2}{r_\mu^5} - \frac{1}{r_\mu^3} \right] S(\vec{r}_\mu) \, d\vec{r}_\mu \tag{3.11}$$

The spin density $S(\vec{R})$ for a N-body system is rigorously defined as:

$$S(\vec{R}) = 2 \int \Psi^*(x_1, \cdots x_N) \ \hat{S}_z(\vec{R}) \ \Psi(x_1 \cdots x_N) \, dx_1 \cdots dx_N \tag{3.12}$$

where, as before, x_i represents the space-spin co-ordinates (r_i, σ_i), Ψ is the Slater determinant of one-electron orbitals $\phi_1(x_1) \cdots \cdots \phi_N(x_N)$ and $\hat{S}_z(\vec{R})$ is the z-component of the total spin operator at point $\vec{R}$ given by:

$$\hat{S}_z(\vec{R}) = \sum_{i=1}^{N} s_{iz} \, \delta(\vec{r}_i - \vec{R}) \tag{3.13}$$

Substituting (3.13) into (3.12) and using orthonormality of the ϕ_i's and the fact that

$$s_{iz} \begin{cases} \alpha_i \\ \\ \beta_i \end{cases} = \pm \frac{1}{2} \begin{cases} \alpha_i \\ \\ \beta_i \end{cases}$$

where α and β are the spin up and spin down eigenfunctions respectively, the N-body spin density becomes:

$$S(\vec{R}) = \left\{ \sum_{\text{spin up}} | \phi_i(\vec{R}) |^2 - \sum_{\text{spin down}} | \phi_i(\vec{R}) |^2 \right\} \tag{3.14}$$

In a one-electron (pseudopotential, for example,) or a RHF calculation (when spin up and spin down form equivalent pairs), the spin density as expressed in (3.14) reduces to the square of the amplitude of the unpaired orbital. In the UHF formalism, on the other hand, because of spin polarization effect explained earlier (section 2.3), orbitals other than the unpaired one may start to contribute. This can be seen clearly from (3.14).

The self-consistent solution of the cluster Fock equation produces a set of ϕ_i's from which $S(\vec{R})$ can be calculated, from which the isotropic hfs constant "a" in (3.7) and the axially symmetric anisotropic hfs constant "b" in (3.11) can be evaluated. "a" is calculated exactly in this way while the integral involved in "b" is difficult to compute without further approximations. We followed the same approximations made by Harker[18] in his pseudopotential calculation. Writing out $|\phi_i|^2$ in terms of the basis functions, we have

$$|\phi_i|^2 = \sum_{\nu=0}^{6} \sum_{\nu'=0}^{6} \sum_{j=1}^{M_\nu} \sum_{j'=1}^{M_{\nu'}} C_{\nu j} C_{\nu' j'} \chi_{\nu j} \chi_{\nu' j'} \qquad (3.15)$$

where the summation index $\nu = 0$ refers to the vacancy while $\nu = 1$ to $\nu = 6$ refers to lthe six N.N. to the vacancy, M_ν and $M_{\nu'}$ are the number of atomic orbitals centred on the ν-th and ν'-th sites, $\chi_{\nu j}$ is the Gaussian atomic orbital (primitive or contracted) and $C_{\nu j}$ is the self-consistent variational coefficients. If (3.15) is substituted into (3.11), many integrals of the form:

$$\int d\vec{r}_\mu \; \chi_{\nu j} \left[\frac{3 z_\mu^2}{r_\mu^5} - \frac{1}{r_\mu^3} \right] \chi_{\nu' j'} \qquad (3.16)$$

will appear. Here, the suffix μ denotes the nucleus at $\vec{R}_\mu$, for which we want to calculate the hfs constant. Because of the r_μ^{-3} dependence, the integrand in (3.16) will be strongly localized about $\vec{R}_\mu$. Therefore, we ignore all terms except the ones with $\nu = \nu' = \mu$ and $\nu = \nu' = 0$ (the vacancy). The approximation amounts to considering the electronic structure of the μ-th ion and the F-electron only. The second class of integral is still difficult to evaluate. We made the further approximation:

$$\int d\vec{r}_\mu \; \chi_{oj} \left[\frac{3 z_\mu^2}{r_\mu^5} - \frac{1}{r_\mu^3} \right] \chi_{oj'}$$

$$\approx \left[\frac{3 \bar{z}^2}{R_\mu^5} - \frac{1}{R_\mu^3} \right] \int_{r < R_\mu} d\vec{r} \; \chi_{oj} \chi_{oj'} \qquad (3.17)$$

where $\bar{z}_\mu$ is the z-coordinate of the μ-th nucleus and the integration is over a spherical region of radius R_μ about the vacancy. In effect, the interaction of the F-electron with the μ-th nucleus has been approximated as a classical dipole-dipole interaction, with the electronic magnetic moment weighted by the amount of charge within the vacancy. With these assumptions, the final expression for "b" becomes:

$$b_\mu = \frac{g_e \mu_B g_N \mu_N}{2 \hbar} \left\{ \sum_{jj'} C_{oj} C_{oj'} \left[\frac{3 \bar{z}_\mu^2}{R_\mu^5} - \frac{1}{R_\mu^3} \right] I_{jj'}^{(0)} \right.$$

$$\left. + \sum_{jj'} C_{\mu j} C_{\mu j'} I_{jj'}^{(\mu)} \right\} \qquad (3.18)$$

where
$$I_{jj'}^{(0)} = \int_{r < R_\mu} d\vec{r} \; \chi_{oj} \; \chi_{oj'} \tag{3.19}$$

$$I_{jj'}^{(\mu)} = \int d\vec{r}_\mu \; \chi_{\mu j} \left[\frac{3 \zeta_\mu^2}{r_\mu^5} - \frac{1}{r_\mu^3} \right] \chi_{\mu j'} \tag{3.20}$$

The hfs constants a and b for the nearest neighbour are now readily calculated, using (3.7), (3.14) and (3.18). These quantities have also been unambiguously determined experimentally by the Electron-Nuclear-Double Resonance (ENDOR) technique [55],[56],[57] with which the theoretical values can be compared. The results for the isotropic hfs constant a are listed in Table 6 while that for the anisotropic hfs constant b are listed in Table 7.

3.2.3   Spin-Polarization

The effect of spin polarization and the need for a UHF formalism have been discussed in the previous sections. Here, we display some of the relevant data to assess its importance.

Fig. 5 shows the orbital energies of the spin up and spin down orbitals in LiF. The shifting of one set of orbital energies relative to the other is a qualitative measure of the effect of spin polarization on the energetics. Fig. 6 shows the same thing in KCl. Since UHF molecular orbitals are not necessarily symmetry orbitals, it is more appropriate to retain the atomic notation in their designation, rather than using the notation according to the irreducible

Table 6

Isotropic hfs constants "a" for the nearest
neighbour of F-centre in alkali halides.
Results are given for ^{7}Li and ^{39}K in units
of MHz. The various symbols are explained
in Table 5. The BSG values are taken from
Harker in Ref. 18.

	GA	BSG	UHF	Experiment
LiF	101.0	93.6	61.29	38.15
LiCl	22.5	38.2	32.76	19.1
LiBr	15.0	32.1	26.83	--
LiI	7.0	17.1	21.15	--
KF	49.7	51.3	18.56	34.3
KCl	24.7	28.4	8.23	20.7
KBr	19.9	21.8	7.32	18.2
KI	13.6	17.3	5.90	15.1

Table 7

Axially symmetric anisotropic hfs constants
"b" at the nearest neighbours of F-centres
in alkali halides. Results are given for
^{7}Li and ^{39}K in units of MHz. The various
symbols are explained in Table 5. The BSG
values are taken from Harker in Ref. 18.

	GA	BSG	UHF	Experiment
LiF	3.45	3.55	2.79	3.2
LiCl	1.90	1.80	1.95	1.72
LiBr	1.50	1.50	1.38	--
LiI	1.20	1.20	0.85	--
KF	1.55	1.45	1.42	1.6
KCl	0.78	0.75	0.57	0.94
KBr	0.65	0.66	0.43	0.77
KI	0.48	0.47	0.29	0.62

representations of the nuclear point group. Thus, a 1s-like
orbital is one which is formed from linear combinations of
1s atomic orbitals localized on the various nuclei, and so
on.

As for the isotropic hfs constant "a", we can have a
quantitative estimate of the contribution due to spin polar-
ization by taking it as the difference between rigorous UHF
result and the result obtained by using the F-electron orbi-
tal alone.   (This can only give a rough estimate because in
an RHF calculation, although the net contribution does come
from the F-electron orbital alone, it can be different from
the UHF orbital because of the equivalence constraint in the
former).   The results are shown in Table 8.   Fig. 7 is a
plot of the UHF spin densities and the square of the ampli-
tude of the F-electron orbital along the (001) direction in
LiF. The effect of spin polarization shows up clearly with-
in the region of the Li^+-ion.   Fig. 8 shows the same plot
for KCl.   Note the extra wriggles which are due to the or-
thogonality constraint of the more complicated electronic
structure of the K^+-ion.

Fig. 5 and Fig. 6

Orbital energy spectra of the ground states

of the F-centre in LiF and KCl.

The relative shift of the spin-down spectrum

from the spin-up spectrum is an indication

of spin polarization.

The number associated with each level is the

degeneracy of that level.   "F" is the level

of the F-electron.

SPIN UP   SPIN DOWN

ENERGY (a.u.)

−0.204

F ———

−0.208

−0.212

−0.216

−2.336

−2.340

−2.344

−2.348

                                    ≡

−2.352 ≡ 2
        — 3
        — 1

SPIN UP

SPIN DOWN

-0.166

F

-0.170

-1.086

3

3p

5

-1.090

3

-1.094

-1.098

ENERGY (a.u.)

-1.102

-1.104

1

-1.882

5

3s

-1.890

1

-1.892

-12.446

1 2

2p

3

1

-12.450

-15.171

5

2s

-15.173

1

-134.824

-134.826

1s

5

1
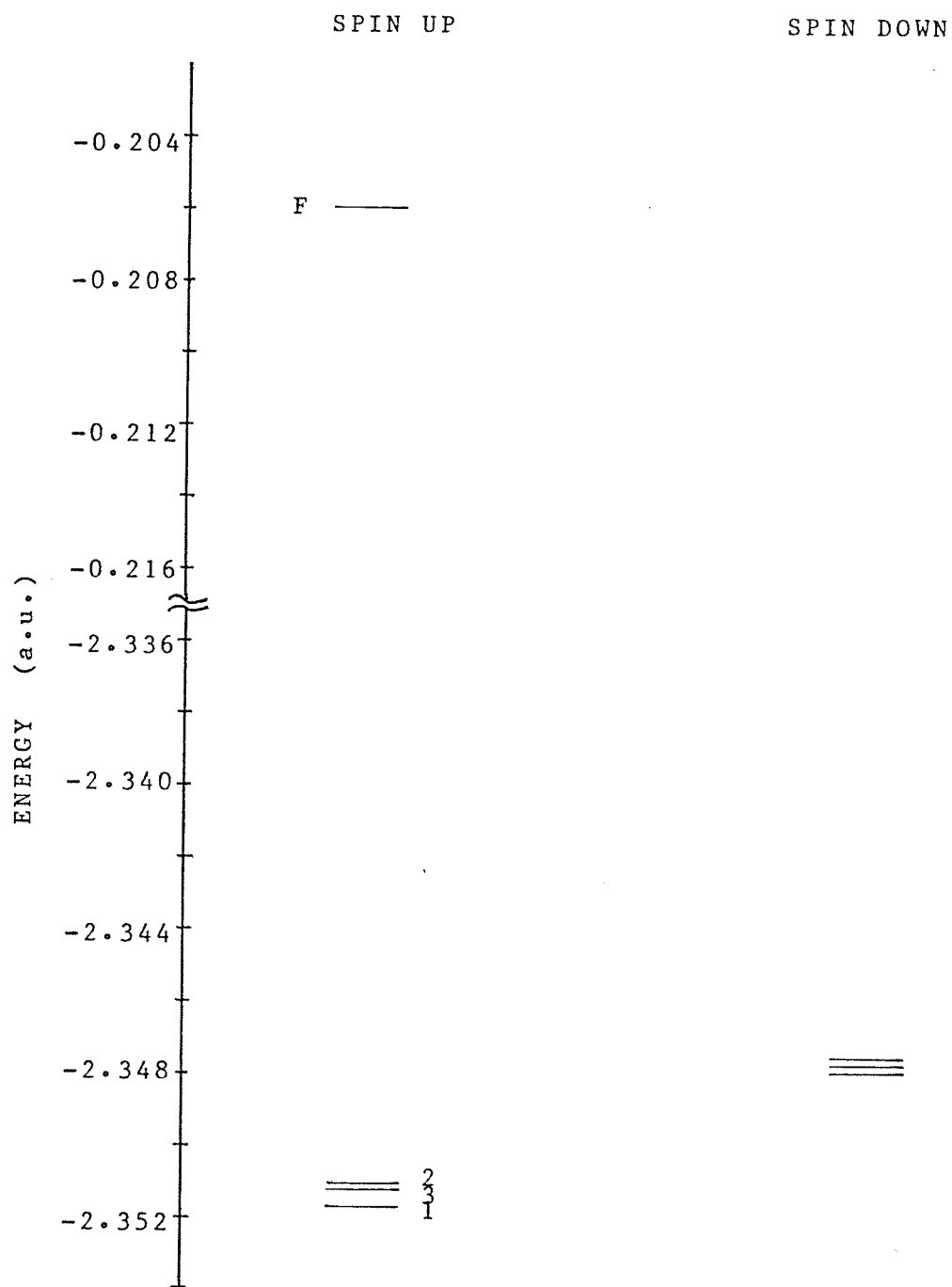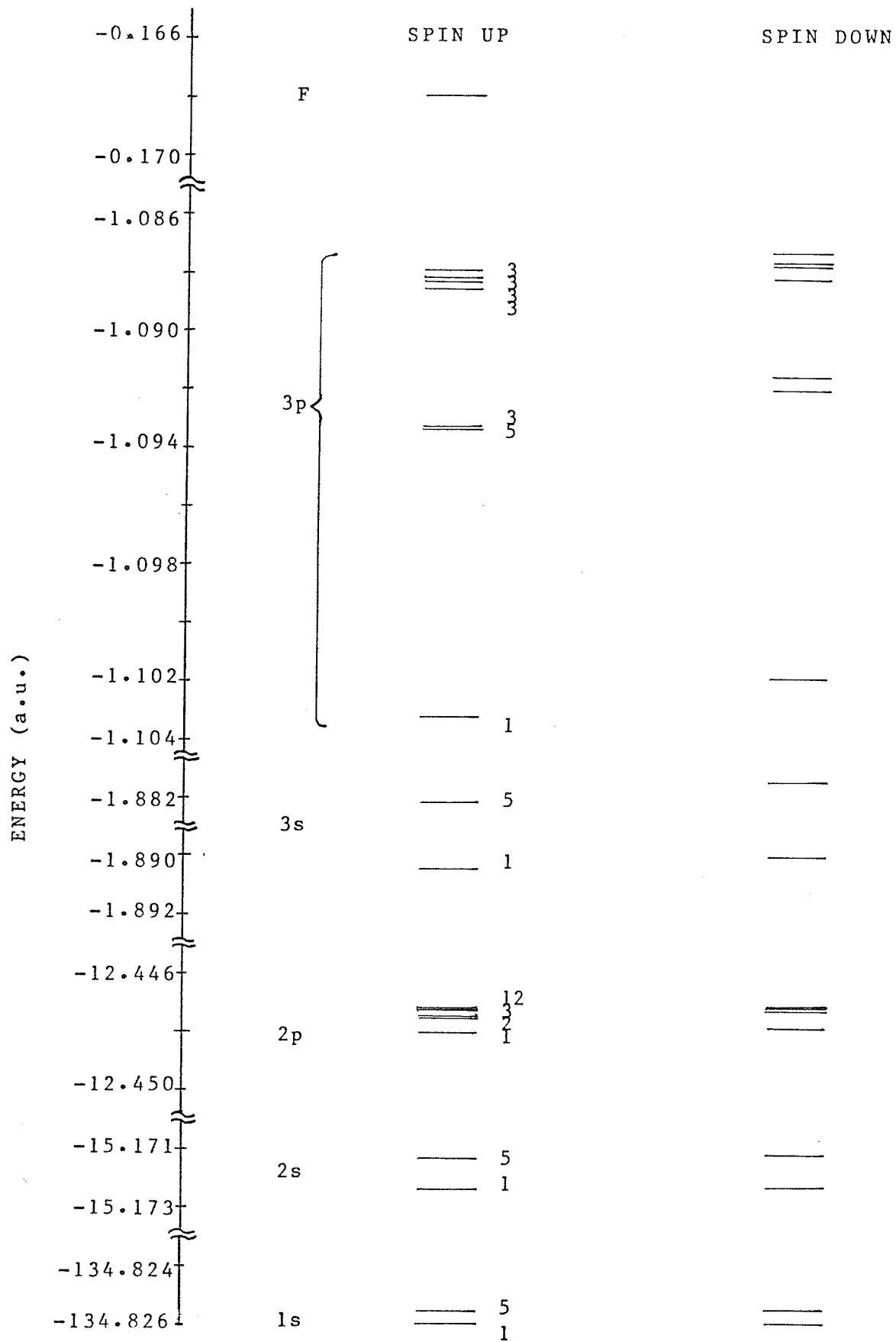
Table 8

Spin polarization effects at nearest neighbour of F-centres in alkali halides.
$S(001)$ and $|\phi_F(001)|^2$ are the spin density and F-electron amplitude squared at (001) in atomic units. P is the corresponding spin polarization. The numbers in the brackets are corresponding quantities in units of MHz.

	$S(001)$	$|\phi_F(001)|^2$	$P = S - |\phi_F|^2$	
LiF	0.03530	0.02866	0.00664	(11.517)
LiCl	0.01892	0.01452	0.00467	(8.100)
LiBr	0.01545	0.01181	0.00364	(6.314)
LiI	0.01219	0.00926	0.00293	(5.082)
KF	0.08911	0.08296	0.00615	(1.281)
KCl	0.04126	0.04006	0.00120	(0.250)
KBr	0.03516	0.03425	0.00091	(0.190)
KI	0.02832	0.02838	-0.00006	(-0.012)

Fig. 7 and Fig. 8

Spin densities and square of the amplitude
of the F-centre orbital plotted along the
[001]-direction in the ground states of LiF
and KCl.

UHF CALCULATIØN (G64A)

F-CENTRE IN LIF

GRØUND STATE SPIN DENSITY
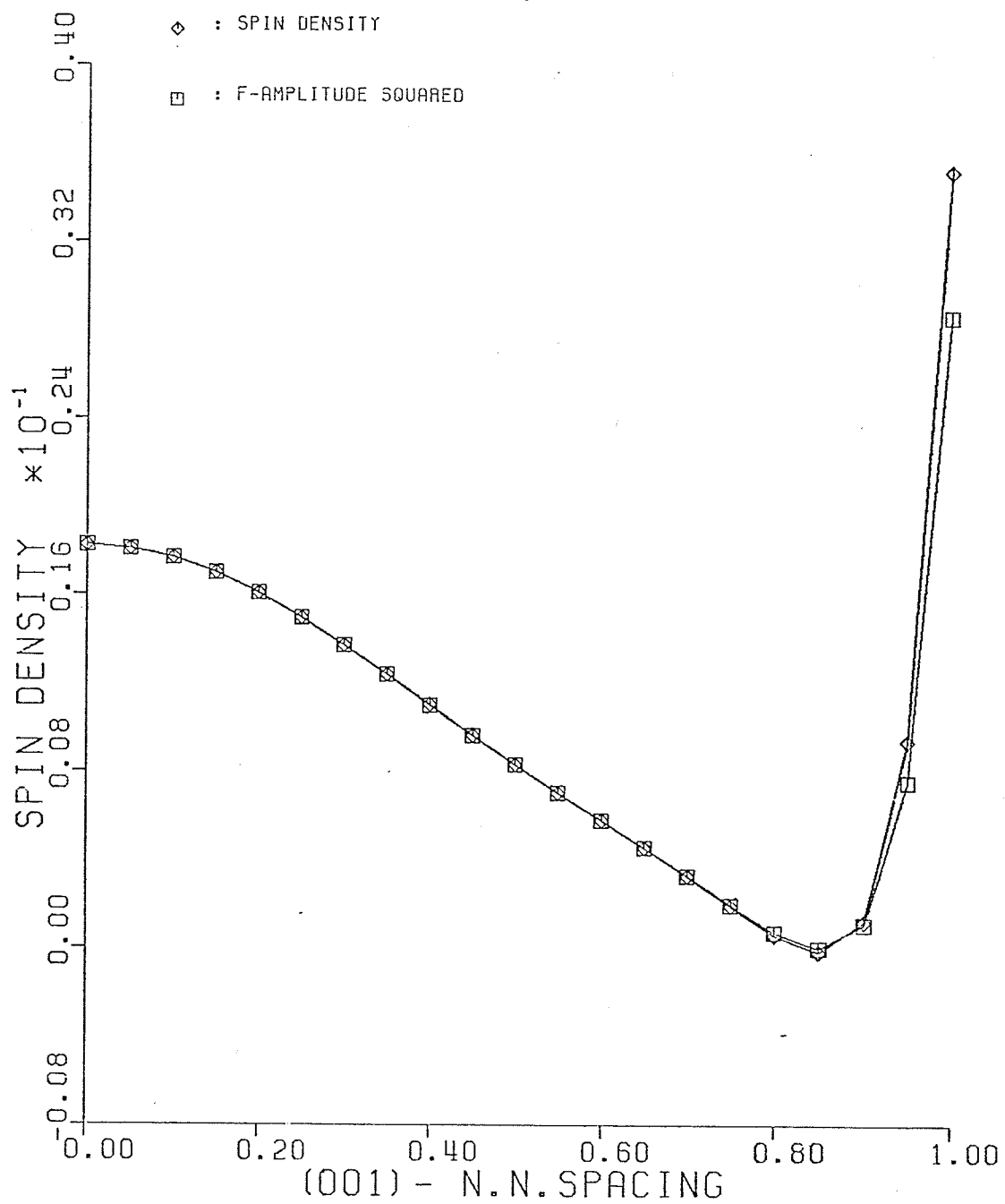
UHF CALCULATION (G82)

F-CENTRE IN KCL

GROUND STATE SPIN DENSITY

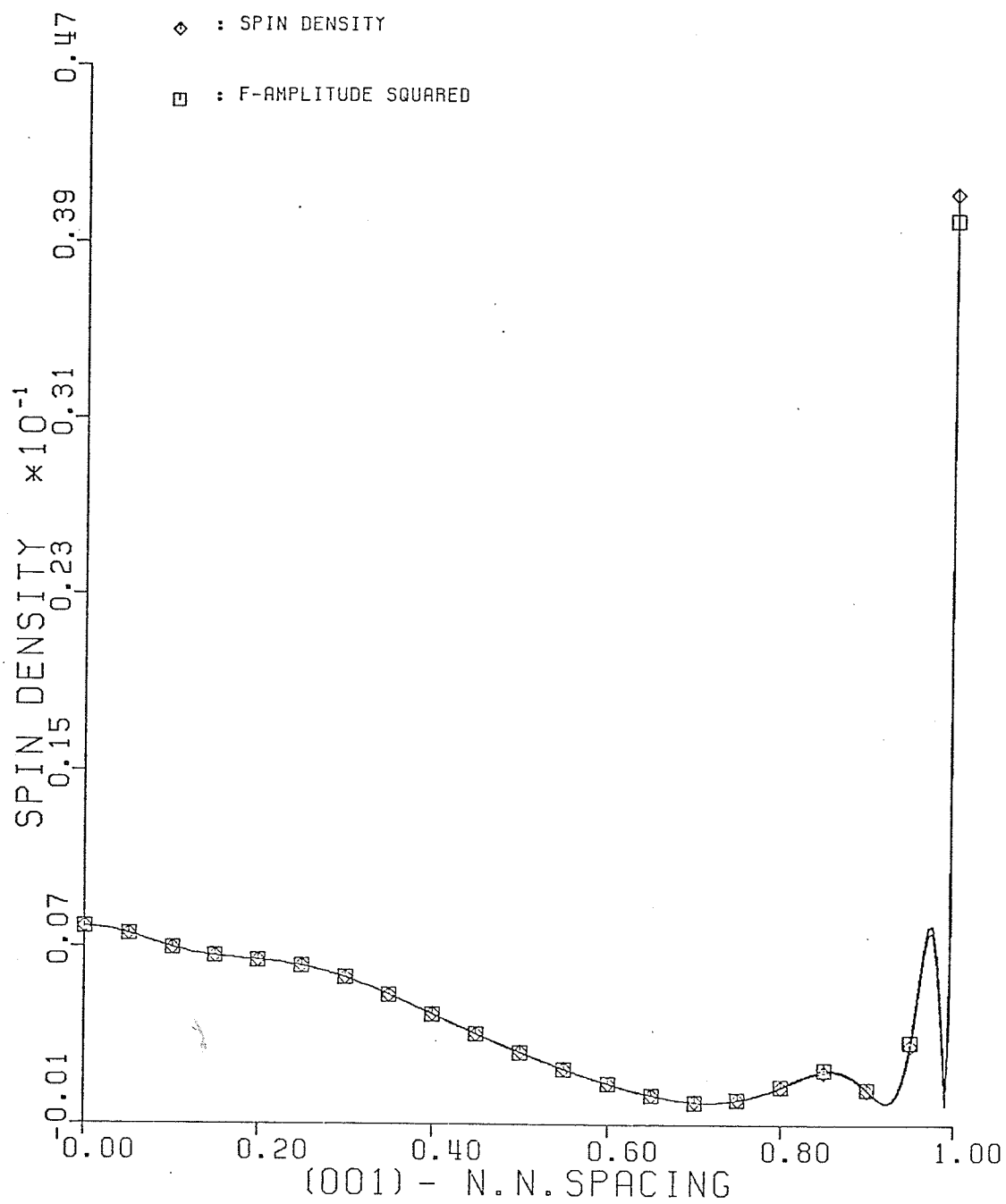## 3.3   RESULTS OF CALCULATIONS ON F_A-CENTRES

3.3.1   Optical Absorption

The characteristics of F_A-centre absorption have been mentioned in section 1.2.2 (see Fig. 2). Here, besides the lowering of symmetry, the situation is further complicated by the fact that the smaller substitutional cation is likely to be displaced significantly from the perfect host lattice site. The exact displacement is unknown, nor is it a good idea to calculate the displacement of the impurity cation alone (say, by minimizing the lattice energy) without considering the relaxation of the rest of the ions since then, the totality of the variational freedom rests on this parameter alone, and the resultant displacement is bound to be too large. For this reason , the calculations are performed with the impurity ion (Li^+ in all of the present cases) undisplaced and then it is repeated for KCl:Li with the Li^+ ion displaced outward (arbitrarily but reasonably) by 0.08 of the N.N. spacing along the symmetry axis. This particular value is taken from the lattice relaxation calculation of Ong and Vail[30]. The changes introduced by the displacement can then be examined.

The computations are done using the same basis set as listed in Table 4 for the K^+ ion, The impurity Li^+ ion is placed on the (010) position, and, six uncontracted GTO of exponents 266.275, 40.048, 9.029, 2.433, 0.711 and 0.048 are used. The ground state is calculated using s-type orbitals

centred at the vacancy. For the F_{A1} and F_{A2}-excited states
(see Fig. 2 on P.23) the entire calculation is repeated us-
ing p_y-orbitals (overlapping the impurity ion) and p_z-orbi-
tals (overlapping the host ions) respectively. The expo-
nents are set to be the same as those listed in Table 4.
The results for KCl:Li and KBr:Li are listed in Table 9.

3.3.2   Hyperfine Interactions

Because of the presence of the Li impurity ion at (010),
the host K^+ ions at $(0\bar{1}0)$ and (001) become inequivalent, and
the corresponding isotropic and anisotropic hfs constants
are different for the three different sites. Using the same
theory as presented in section 3.2.2, these parameters are
calculated for KCl:Li and KBr:Li. The results are shown in
Table 10. The spin densities along the three inequivalent
directions [010], $[0\bar{1}0]$ and [001] in KBr:Li are plotted in
Fig. 9.

3.3.3   Displacement of Li^+ ion

To see the effect of the displacement of the impurity
Li^+ion, the calculations were repeated for KCl:Li with the
Li^+ion displaced by 0.08 of N.N. spacing away from the va-
cancy along the symmetry axis (y-axis). The results are
shown in Table 11. The previous results of undisplaced Li^+
are also shown alongside for convenience of comparison.

Table 9

Optical absorption of F_A-centres in KCl:Li and KBr:Li. The Li^+ ion is at perfect host lattice site.
ΔE_1 and ΔE_2 are the F_{A1} and F_{A2} transition energies respectively. δ is the $F_{A1}-F_{A2}$ splitting. Energies are in units of eV. The numbers inside the brackets are corresponding experimental values taken from Luty, Ref. 27.

	ΔE_1	ΔE_2	δ
KCl:Li	2.26 (1.98)	2.48 (2.25)	0.22 (0.27)
KBr:Li	1.89 (1.82)	2.10 (2.00)	0.21 (0.18)

Table 10

Isotropic hfs constants "a" and anisotropic
hfs constants "b" in KCl:Li and KBr:Li.
"a" and "b" are in units of MHz. K_α is the
host K^+ ion on the symmetry axis (the axis
joining the F-centre and the impurity Li^+
ion) while K_β is the host K^+ ion perpendicu-
lar to the symmetry axis. Experimental data
for KCl:Li are quoted from Mieher[58], and
for KBr:Li are quoted from Watanabe, Mori
and Ohkura[59].

		KCl:Li		KBr:Li	
		UHF	Experiment[58]	UHF	Experiment[59]
a(Li)		23.74	7.88	21.90	6.93
a(K_α)		7.83	23.71	5.85	22.41
a(K_β)		7.83	23.36	6.66	21.09
b(Li)		0.95	0.63	0.79	0.58
b(K_α)		0.52	0.99	0.40	0.84

Fig. 9

Spin densities plotted along the [010], [0$\bar{1}$0] and [001] directions in KBr:Li to show the asymmetry due to the presence of the impurity Li$^+$ion.

◇ : [010] direction

◻ : [0$\bar{1}$0] direction

△ : [001] direction

UHF CALCULATIØN (G75)
FA-CENTRE IN KBR:LI
GRØUND STATE SPIN DENSITY
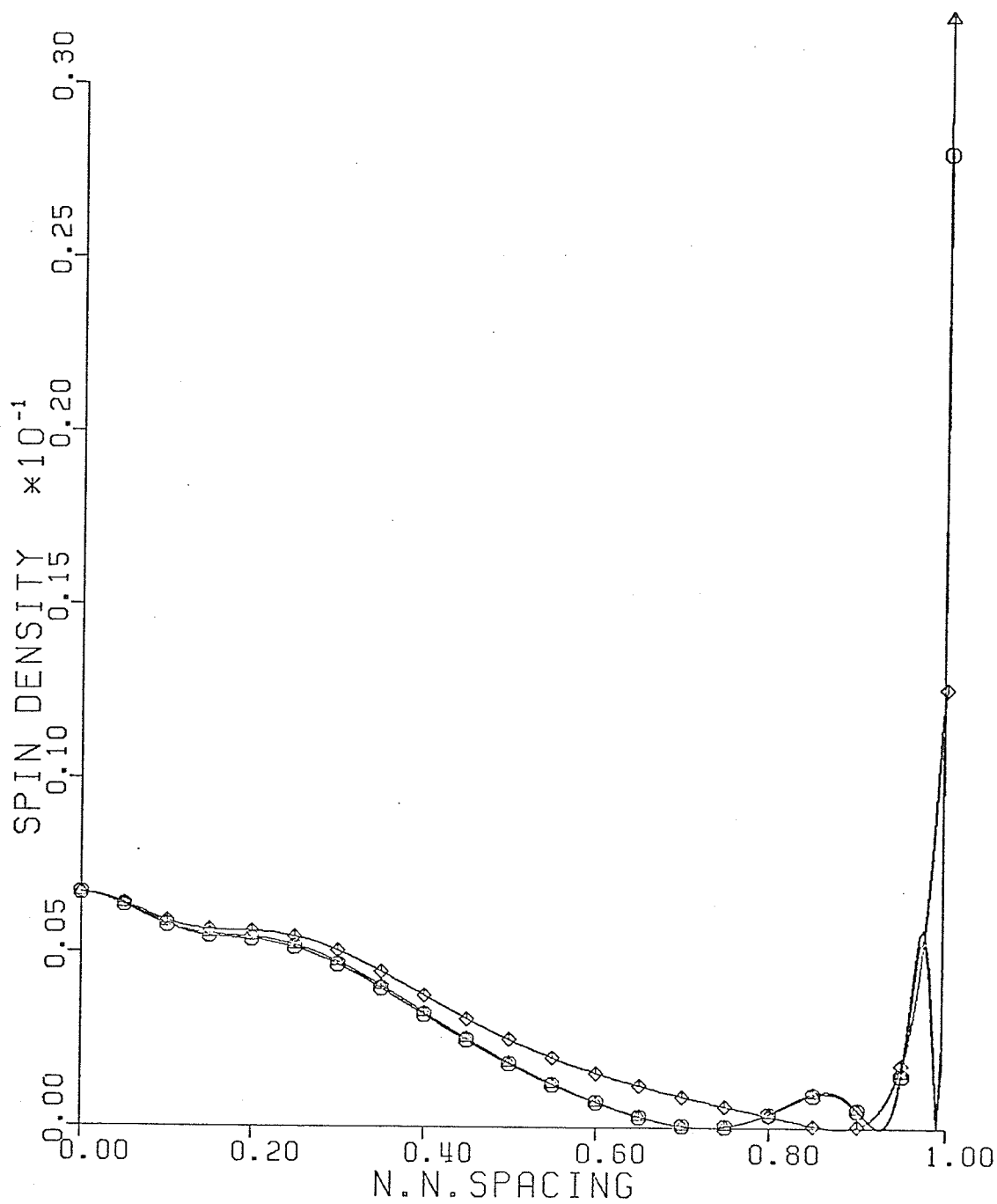
Table 11

Comparison between results of calculations with an undisplaced and displaced Li^+ ion in KCl:Li. The displacement is 0.08 of N.N. spacing outward along the symmetry axis. The various symbols have the usual meanings as explained in the previous Tables. Energies are in units of eV. and hfs parameters are in units of MHz.

	KCl:Li		
	undisplaced	displaced	Experiment
ΔE_1	2.26	2.17	1.98
ΔE_2	2.48	2.34	2.25
δ	0.22	0.17	0.27
a(Li)	23.74	15.91	7.88
a(K_α)	7.83	7.93	23.71
a(K_β)	7.83	8.54	23.36
b(Li)	0.95	0.78	0.63
b(K_α)	0.52	0.52	0.99

Chapter IV

DISCUSSION AND CONCLUSION

On account of the theory presented in Chapter 2, it is clear that the cluster method used here can actually be looked at as a kind of ab-initio extended ion calculation where the electronic structure of the first N.N. is self-consistently taken into account. This differs from the previous work along similar lines e.g., Wood and Joy (WJ), Ref.(13) in an important aspect, namely that self-consistent core readjustment in both the ground and excited states is fully incorporated in the UHF level of treatment. (This was referred to as level 1 in the discussion in Chapter 1, P.5). The results of the present calculations, as presented in Chapter 3, mostly speak for themselves. A qualitative summary, as well as their implications, are given below.

4.1   F-CENTRES

We believe that the basis set used in this calculation is fairly extensive, and that it has sufficient variational flexibility.

The calculated absorption energies agree quite well with experiment, with the exception of LiF. This is evident from the Ivey-Mollwo plot as shown in Fig. 4. With reference to

Table 5, P.61, we note that the UHF absorption energies are not very much different from those obtained from the extended-ion calculations of WJ. It seems, then, that core readjustment is not particularly important in the F-centre absorption process. Further, the low absorption energy of LiF obtained by both WJ and the present UHF calculation seem to indicate the deficiency of neglecting the electronic structures of ions more distant than the N.N., since, in somewhat similar calculations when further shells of neighbours are included (e.g., Leung and Song[16], Chaney and Lin[35], Tennyson and Murrell[65],[66] (see epilogue)) results which agree fairly well with experiment are obtained. All theoretical efforts fail to yield the apparently anomalous experimental absorption energy of LiI, but there have been reservations about the accuracy of this experimental value[60].

The theoretical prediction of the isotropic hfs constant "a" has long been recognised to be an extremely difficult task because it depends on the wavefunction at one spatial point only, i.e., $\left| \Psi(\vec{R}_{\nu}) \right|^2$. Thus, "a" is sensitive to almost every parameters in the calculation, and notably so to the chosen basis set. From Table 6, P.69, where the calculated values of "a" are shown, it can be seen that the UHF-cluster method produces results which are too high in the lithium halides and too low for the potassium halides. When compared with the corresponding results obtained by other

theoretical methods (e.g., the BSG pseudopotential method[24],[25], the extended-ion calculations of Wood and Opik[14],[15]), the UHF results are lower in all cases. Although basis set effects may play a part, there is little doubt, however, that the poor agreement of the UHF results with experiment is largely due to neglect of the electronic structure of the second and further nearest neighbours. Wood[17] has demonstrated the importance of this in hfs parameter calculations. In the terminology of the cluster model, it is the neglect of the overlap of the cluster and environment wavefunctions. In this case, the second nearest neighbour halide ions may play an important role since it is well-known that they are quite diffuse in alkali halide crystals. Thus, the UHF cluster results deviate successively further from experimental data with increasing anion size, ranging from 45% in KF to 61% in KI. It is interesting to note that the opposite trend prevails in the BSG calculation.

More or less the same discussion applies to the axially symmetric anisotropic hfs constant "b", as is evident in Table 7, P.70. Here, while the UHF results are lower than the corresponding BSG results, they are also lower than the experimental values in all cases. Again, the electronic structure of the second nearest neighbours may be largely responsible for the discrepancies.

The relevance of UHF calculations for paramagnetic systems and the effect of spin polarization have been advocated before. While it is difficult to have quantitative assessment of its influence on the total energy (unless one repeats the whole calculation with RHF method), Figs. 5 and 6 (P.73 and 74), which illustrate the relative shift of the spin up-spin down orbital eigenvalues, show that it is not negligible. This effect is more pronounced in the lithium halides than in the potassium halides. In LiF, each spin down level is shifted up by about 0.1 eV. from its corresponding spin up level. In KCl, the inner core levels are only very slightly affected while the "3s" and the "3p" levels are shifted by about 0.03 eV. on the average.

Estimates of the contribution of spin polarization to the isotropic hfs constants are shown in Table 8 on P.75. Except for KI, they are all positve, and are approximately 20% in the lithium halides while in the potassium halides, it decreases from about 7% in KF to about -0.2% in KI. Ikenberry et.al.[61] has calculated the same quantity in LiF by a perturbation method using the Gourary and Adrian type III wavefunction[7]. They obtained a value of 15.424 MHz, which is quite close to our estimate of 11.517 MHz. In any case, the present calculation indicates that the neglect of spin polarization is probably tolerable in the potassium halides while it is much less justified in the lithium halides.

In principle, it is also possible to calculate the hfs parameters of the excited state (the spin-orbit coupling constant and the orbital g-factor) of the F-centre with the UHF cluster results. Smith[62],[63] has discussed these in detail. Such calculations, however, are not carried out in the present case for the following two reasons:

(a) The 2p-like excited state of the F-centre is generally more diffuse than the 1s-like ground state. Therefore, the basic assumption of small cluster-environment overlap is not well-justified. Consequently, calculations based on our excited state wavefunction are not expected to be reliable.

(b) Smith in Ref. 62 and 63 has performed extended-ion calculations on the spin-orbit coupling constants and the orbital g-factors respectively, and concluded that the major contributions come from the second nearest neighbours. Since the electronic structures of the second nearest neighbours are ignored in the present work, calculations of these parameters would be further suspect.

Lattice distortion has been ignored in all of the above calculations. However, all theoretical work in the past indicates that distortion in the ground state is insignificant, and if a Frank-Condon type of transition is assumed, the neglect of lattice distortion in the F-centre absorption process is well justified. Likewise, electron-phonon interaction is also ignored, although it may play an important role in the relaxed excited state, its effect is known to be negligible in the ground state and the absorption process.

4.2 F_A-CENTRES

The F_{A1}-F_{A2} splitting in the F_A-centre has long been a challenge in colour centre calculation. Ong and Vail[30] have presented a concise review of this subject. Since the splitting, due to the difference in the electronic structures of the host and impurity cations, is relatively small (around 0.2 eV.), the particular theoretical model must be sufficiently accurate to take detailed account of such differences. It has already been reported in Chapter 1 that the BSG pseudopotential method has not been fully satisfactory in treating this problem. Table 9 on P.81 shows the results of the present calculations on the splittings to be in good agreement with experiment, both in direction and magnitude, and thus demonstrates the fact that the UHF cluster model is capable of dealing with detailed energetics at the ab-initio level.

The calculated values of hfs parameters as shown in Table 10 on P.82 follow more or less the same trend as in the F-centres. As in the F-centres, the calculated isotropic hfs constants for the K^+ ions are too low, probably due to the neglect of the second nearest neighbours. However, it is surprising to see the large discrepancies in the values of a(Li) where the theoretical results are much larger than the experimental[58],[59]. The experimental spin densities at the impurity Li^+ site are rather small. The ratio of the spin densities at the Li^+ site and at the K_α site, given by:

$$\frac{|\Psi(Li)|^2}{|\Psi(K_\alpha)|^2} = \frac{g_N(K_\alpha)\, a(Li)}{g_N(Li)\, a(K_\alpha)}$$

where $g_N(K_\alpha)$: Nuclear g-factor of K^{39} = 0.2606,

and $g_N(Li)$: Nuclear g-factor of Li^7 = 2.1706,

are experimentally 0.040 and 0.037 for KCl:Li and KBr:Li respectively. Both Mieher[58] and Watanabe[59] attributed this to the (fairly substantial) displacement of the Li^+ ion outward from the F-centre along the symmetry axis. With reference to Table 11 on P.85, we see that, according to our calculation although the displacement does lower the value of a(Li), such large "on-axis" displacement as suggested by Mieher and Watanabe et. al's data is unlikely. Moreover, Rosenburger and Luty[64] have shown that, in KCl:Li, the Li^+ ion tunnels between four equivalent off axis sites, based on evidence from electric field modulated absorption experiments. This effect may go some way towards explaining the discrepancies in KCl:Li. The situation in KBr:Li is even less clear, where the Li^+ ion is thought to lie on axis.

The equality of the UHF $a(K_\alpha)$ and $a(K_\beta)$ in Table 10 on P.82 is accidental. Our calculations show that this is due to the balance between the magnitude of the F-wavefunction and spin polarization. At the K_α site, the smaller magnitude of the F-wavefunction (relative to that at the K_β site) is accompanied by a larger contrubution due to spin polarization.

It is evident from Table 11 on P.85 that displacement along the symmetry axis of the impurity Li^+ ion does not change the above discussion qualitatively. $a(K_\alpha)$ and $a(K_\beta)$ are no longer equal but their relative magnitudes are opposite to the experimental data. The same is true for KBr:Li even with the Li^+ undisplaced.

4.3   GENERAL CONSIDERATION ON COMPUTATIONAL SCALE

Early ab-initio molecular/extended-ion calculations suffered from requirement of excessive computer resources because of the huge number of multicentre integrals which have to be evaluated, and the iterative nature of the subsequent solution of the Fock equation. Consequently, simplifying assumptions were made (e.g., Wood and Opik[14],[15]), and the SCF problem was rarely touched upon, except for the cases of atoms and simpler molecules. Today, very efficient codes performing multicentre integration are generally available (at least for GTO), and with the rapid advancement of computer technology, computing capacity which used to be within the reach of the large research laboratories only is now generally possible in any fair sized institute. There is good reason to reassess some of the limitations set by the early work.

All the computations pertaining to the present work were done with the University of Manitoba Amdahl 470/V7 system operating under MVS. The CPU is approximately 2.5 times

faster than an IBM 370/168 and about 1.6 times slower than a CDC 7600. The CDC Cyber 205 and Cray 1-S, which are probably the fastest computers today for scientific and numerical purposes, are about 130 times faster than the Amdahl 470/V7[67]. In a potassium halide F-centre ground state calculation, using the basis set described earlier, some 4,000,000 multicentre two-electron integrals need to be calculated, although with full cubic symmetry, only about 150,000 of these need to be computed from first principles. This takes approximately thirty CPU minutes. The amount of CPU time required to do the SCF calculation, of course, depends on the initial guess but typically it takes another thirty CPU minutes (for about 25 iterations). Thus, the total CPU time required approaches an hour. For systems with lower symmetry, while the computer time required for the SCF calculation remains the same, the requirement for integral evaluation quickly becomes dominant. For example, in the F_{A2} excited state of the F_A-centre, the symmetry is C_{2v} and the integrals would take typically 1.5 CPU hours to compute.

These figures should give an idea of the magnitude of the computations involved. While it can be considered as "substantial" by most installations, it is, nevertheless, quite feasible.

On the other hand, if the electronic structures of the second N.N. are taken into account, for the simple case of F-centre in KF, and using Huzinaga's (11s 6p/4s 2p) CGTO for

the floride ions, the number of basis functions, N, increas-
es from 82 to 202! The CPU time required to perform the SCF
calculation is roughly proportional to N^4, if a calculation
with N=82 took about half an CPU hour, a calculation with
N=202 would take approximately 18 CPU hours! Moreover, with
the dramatic increase in the number of multi-centre inte-
grals, one would certainly run into severe storage problem.
Because of the high symmetry of the F-centre, the CPU time
required to evaluate the additional integrals should be
fairly minor relative to the SCF procedures. However, in
systems of lower symmetry, the computation of the integrals
alone would take an unreasonably large amount of computer
time. Attempts at this level are definitely beyond the ca-
pacity of the computer system here.

4.4   CONCLUSION

We have demonstrated that the UHF cluster method is ca-
pable of giving accurate energetics when applied to colour
centre problems, but fails to yield reliable hfs parameters
due to the neglect of the second (or possibly further) near-
est neighbours. One way to rectify this is to orthogonalize
the resultant cluster wavefunction to neighbouring ionic wa-
vefunctions. The latter can be obtained from a separate
cluster calculation, or if less accuracy is required, simply
taken as free-ion HF wavefunctions. The hfs parameters
could then be recalculated.

We hope that the present work will serve as a starting point for further _ab-initio_ studies in colour centre problems, leading to reliable results where experimental data are less readily available.

EPILOGUE

After the completion of the present calculations, and with this manuscript half written, it has come to our attention that there have been two recent calculations on the absorption energy of the F-centre in LiF by Murrell and Tennyson[65],[66]. These authors have performed *ab-initio* RHF calculations using the ATMOL3 program documented by the Rutherford Laboratory, Didcot, England, and the electronic structures up to the third nearest neighbours are included. In the former reference, the absorption energy is found to be 3.2 eV. compared with the experimental value of 5.13 eV., while in the latter, with improved Madelung potential and enlarged basis set, it is found to be 4.6 eV. However, if only the electronic structures of the first nearest neighbours are included, the absorption energy is 3.6 eV. It is gratifying to see that, although using very different computer programs, there is close agreement between our results, namely 3.54 eV. vs. 3.6 eV.

We are grateful to Dr. A.H. Harker of AERE, Harwell, England, who drew our attention to these papers.

APPENDIX

The UHF-Series Programs

The computer codes used in performing the UHF calculations in the present work are based on the UHF series programs collected in the MQM library in the Material Science Research Laboratory, University of Illinois, Urbana-Champaign. It involves three programs running in sequence. The functions of each of them are briefly described below:

(1) LABEL: The user inputs the transformation properties of the basis functions under the symmetry operations of the point group to which the basis set belongs. By considering this symmetry information, "LABEL" then generates a set of unique integrals which are to be calculated. The rest are, by symmetry, either zero or set equal to positive or negative of the unique integrals.

(2) POLYIN: The information on the nuclei and basis functions (exponents, contractions, etc.) are detailed. POLYIN handles only Gaussian type basis functions (primitive or contracted) and they are limited to be s, p, d and f types. With the symmetry information generated by LABEL, all the multicentre integrals are evaluated and stored.

(3) UHF: This program performs the self-consistent field calculation. The user specifies the number of spin up and spin down orbitals to be occupied and inputs the initial guess of the transformation matrix to start the iteration.

The algorithm has already been discussed in the text (see P.49-50). Besides solving the SCF equation, UHF also performs Mulliken population analysis over the basis functions.

The Illinois version of the UHF-series programs is tailored to run in a DEC-20 machine. There, the primary concern is with main core storage requirement. Thus, amongst other things, the indices of each integral are "PACKed", and complicated array overlaying technique is used for dynamic allocation. In adapting the program to run in the University of Manitoba system (Amdahl 470/V7 operating under MVS), apart from the task of converting the entire program series into "IBM FORTRAN", there is the hardware difference of the 36-bit-word in the DEC machine versus the 32-bit-word in the Amdahl. This difference in word length causes particular difficulty in the "PACKing" of the integral labels. In order to accomodate the larger value of the integral indices as demanded by the present calculation, a different packing scheme, based on combinatorial method, is used, rather than the usual bit-shifting operations. Under the new scheme, indices as large as 84 can be packed.

Other modifications to the original program are listed below:

(1) The maximum number of nuclear centres is raised to 343.

(2) The maximum number of basis functions is raised to 84.

(3)   The maximum number of primitive gaussians is raised to 300.

(4)   More options in printing and in population analysis.

(5)   Interrupt timers are set up in various places and all programs are made restartable.   This is essential because there is a ceiling for the CPU time allowed for a job in the installation here.

(6)   The original convergence criterion (as described on P.50) is very inefficient in handling cases when there are a large number of orbital degeneracies.   An alternative convergence criterion, based on the difference in the total energies between successive iterations, is implemented to deal with these cases.

The load-modules of the Manitoba version of the UHF-series programs are stored on disk in user-library "KUNG.HFPAC".   The documentation pertaining to these programs can be obtained by consulting Prof. J.M. Vail of the Physics Department.

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