CALCULATION OF Z-CENTER ENERGY LEVELS

by

WILBUR VANCE JOHNSON

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1961
APPROVED

Professor of Chemistry

In Charge of Major

Chairman of Department of Chemistry

Chairman of School Graduate Committee

Dean of Graduate School

Date thesis is presented August 16, 1960

Typed by Janice R. Johnson
DEDICATED IN MEMORIAM

TO MY FATHER

REV. GORDON VANCE JOHNSON

Who, more than anyone else, looked forward to the day when this work would be completed, but grew weary and departed on the very day the final typing was begun. Truly he was a constant counselor and faithful friend.

"There is a prince and a great man fallen this day."

II Sam. 3:38
ACKNOWLEDGMENTS

The author wishes to thank Professor Allen B. Scott for suggestion of this problem and for a number of helpful discussions.

He is deeply indebted to Mr. Robert Drusts for spending the midnight-to-dawn hours of many a spring morning putting parts of this problem on the computer.

The cooperation of Professor Shigehiro Kobayashi in expeditiously supplying tables of his solutions of the Thomas-Fermi equation for positive ions is gratefully acknowledged.

Finally, the author expresses his sincere gratitude to his wife, Janice Lynn Johnson, for the endless encouragement and selfless support which alone made completion of this thesis possible.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Color Centers in Pure Alkali Halide Crystals</td>
<td>1</td>
</tr>
<tr>
<td>Color Centers in Alkali Halide Crystals Containing Intentionally Added Alkaline Earth Impurities</td>
<td>1</td>
</tr>
<tr>
<td>Summary of original work</td>
<td>1</td>
</tr>
<tr>
<td>Models proposed for Z centers</td>
<td>4</td>
</tr>
<tr>
<td>Outline of later experiments</td>
<td>5</td>
</tr>
<tr>
<td>Objective and Scope of the Present Work</td>
<td>10</td>
</tr>
<tr>
<td>II. PRELIMINARY CALCULATIONS</td>
<td>13</td>
</tr>
<tr>
<td>Interstitial Point Charge</td>
<td>13</td>
</tr>
<tr>
<td>Expression for the field</td>
<td>13</td>
</tr>
<tr>
<td>Derivation of equations and results</td>
<td>15</td>
</tr>
<tr>
<td>Optical transition energy</td>
<td>17</td>
</tr>
<tr>
<td>Substitutional Point Charge</td>
<td>19</td>
</tr>
<tr>
<td>Comparison with interstitial point charge</td>
<td>19</td>
</tr>
<tr>
<td>Field inside the cavity</td>
<td>21</td>
</tr>
<tr>
<td>Calculation of the effective dielectric constant</td>
<td>22</td>
</tr>
<tr>
<td>Derivation of equations and results</td>
<td>24</td>
</tr>
<tr>
<td>Substitutional Distributed Charge</td>
<td>27</td>
</tr>
<tr>
<td>An artificial potential energy function</td>
<td>27</td>
</tr>
<tr>
<td>Cation in vacuum</td>
<td>29</td>
</tr>
<tr>
<td>Cation in a crystal</td>
<td>30</td>
</tr>
<tr>
<td>Empirical correction term</td>
<td>31</td>
</tr>
<tr>
<td>Approximation of the field outside the cavity</td>
<td>33</td>
</tr>
<tr>
<td>Conclusions</td>
<td>35</td>
</tr>
<tr>
<td>III. CALCULATIONS BASED ON THE THOMAS-FERMI MODEL OF POSITIVE IONS</td>
<td>37</td>
</tr>
<tr>
<td>Thomas-Fermi Equation</td>
<td>37</td>
</tr>
<tr>
<td>Analytic Approximation of Kobayashi's Numerical Solutions</td>
<td>40</td>
</tr>
<tr>
<td>Preliminary result</td>
<td>40</td>
</tr>
<tr>
<td>Least squares refinement</td>
<td>43</td>
</tr>
<tr>
<td>Modification of the Thomas-Fermi Radius</td>
<td>48</td>
</tr>
<tr>
<td>Polarization</td>
<td>53</td>
</tr>
<tr>
<td>Approximations for p and the Field outside the Cavity</td>
<td>60</td>
</tr>
<tr>
<td>Derivations and Results</td>
<td>64</td>
</tr>
<tr>
<td>Alternate Derivations</td>
<td>70</td>
</tr>
<tr>
<td>Chapter</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>IV. DISCUSSION</td>
<td>79</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>82</td>
</tr>
<tr>
<td>APPENDIXES</td>
<td></td>
</tr>
<tr>
<td>I. Constants Used in Computations and Their Sources</td>
<td>85</td>
</tr>
<tr>
<td>II. Polynomial Coefficients</td>
<td>86</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Experimental Z-Band Energies</td>
<td>9</td>
</tr>
<tr>
<td>2.</td>
<td>Energy Levels of Interstitial Divalent Cations</td>
<td>17</td>
</tr>
<tr>
<td>3.</td>
<td>Optical Transition Energies of Interstitial Divalent Cations</td>
<td>19</td>
</tr>
<tr>
<td>4.</td>
<td>Effective Dielectric Constants</td>
<td>24</td>
</tr>
<tr>
<td>5.</td>
<td>Energy Levels of Substitutional Cations</td>
<td>27</td>
</tr>
<tr>
<td>6.</td>
<td>Constants for Analytic Potential Expression</td>
<td>48</td>
</tr>
<tr>
<td>7.</td>
<td>Constants (Atomic Units) for Analytic Potential Function</td>
<td>65</td>
</tr>
<tr>
<td>8.</td>
<td>Constants in $W_{nl}$ Expression</td>
<td>68</td>
</tr>
<tr>
<td>9.</td>
<td>Variation Parameters and Energies</td>
<td>69</td>
</tr>
<tr>
<td>10.</td>
<td>Constants in $W_{nl}$ Expression</td>
<td>70</td>
</tr>
<tr>
<td>11.</td>
<td>Variation Parameters and Energies</td>
<td>70</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Z Bands in KC1:Sr (after Pick)</td>
<td>3</td>
</tr>
<tr>
<td>2. Z-Center Models</td>
<td>6</td>
</tr>
<tr>
<td>3. Potential Functions for Ca$^{+2}$</td>
<td>54</td>
</tr>
<tr>
<td>4. Potential Functions for Sr$^{+2}$</td>
<td>55</td>
</tr>
<tr>
<td>5. Radial Distribution Functions for Ca$^+$ in KC1</td>
<td>71</td>
</tr>
<tr>
<td>6. Radial Distribution Functions for Sr$^+$ in KC1</td>
<td>72</td>
</tr>
<tr>
<td>7. Radial Distribution Functions for Ca$^+$ in NaCl</td>
<td>73</td>
</tr>
<tr>
<td>8. Radial Distribution Functions for Sr$^+$ in NaCl</td>
<td>74</td>
</tr>
</tbody>
</table>
Color Centers in Pure Alkali Halide Crystals
(25, p. 384-386, 389-392)

Although pure alkali halide crystals are transparent in the visible region, coloration can be introduced in several ways. Among these are bombardment by cathode rays, electrolysis, exposure to x-rays, and heating in the presence of alkali metal vapor. The last method, referred to as additive coloration, is the most common in the present context. The absorption band resulting from additive coloration is called the F band; the sites at which the absorption act occurs are called F centers. At the present time it is generally accepted that the F center consists of an electron trapped at a negative-ion vacancy.

Color Centers in Alkali Halide Crystals Containing Intentionally Added Alkaline Earth Impurities
(21; 22; 24; 26, p. 91-92)

Summary of original work

Potassium chloride crystals containing intentionally added alkaline earth chloride impurities (doped crystals) color like the pure crystals, although Pick points out that coloration is at least five times faster in these doped crystals than in the undoped. Illumination in the F band at room temperature partially destroys the F band and develops a new band, slightly displaced to the
long-wavelength side of the F band, called the \( Z_1 \) band. \( Z_1 \) centers are very stable to light at or below room temperature, but above 110°C the \( Z_1 \) band disappears completely, even in the dark, enhancing the F band and producing a new band, called the \( Z_2 \) band, which lies even farther to the long-wavelength side of the F band. Above 200°C the \( Z_2 \) band also disappears, and the F band reappears on quenching. When a crystal containing F and \( Z_2 \) centers is illuminated in either the F or the \( Z_2 \) band at about -90°C, both bands diminish, and the \( F' \) band and another broad band, the \( Z_3 \) band, appear. The latter is similar in appearance to the \( F' \) band but, unlike it, lies on the short-wavelength side of the F band. Both the F and \( Z_2 \) bands are observed to decrease together, regardless of which received the illumination.

The \( F' \) band, like the F band, appears in pure alkali halide crystals, but none of the Z bands does. The \( F' \) center is generally considered an F center plus a second trapped electron, but the exact nature of the various Z centers still remains a subject of some discussion. Typical absorption spectra of strontium-doped potassium chloride crystals are illustrated in Figure 1.

With sodium chloride crystals to which has been added some strontium chloride, the experimental situation is somewhat modified. After these crystals have been quenched from the coloring temperature, they display both the F and the \( Z_2 \) bands. Illumination in the \( Z_2 \) band leads to formation of the \( Z_1 \) band. X-irradiation of strontium-doped, uncolored sodium chloride crystals produces the
Fig. 1. Z bands in KCl:Sr (after Pick)
Models proposed for Z centers

The first to propose models for these three Z centers was Pick (21, p. 81). He suggested that the $Z_1$ center is an electron trapped at an impurity complex, an aggregate consisting of a positive-ion vacancy bound to a divalent cation. Since this center has a negative charge, he feels that a rise in temperature will cause the positive-ion vacancy to diffuse away, leaving the electron trapped by the unassociated divalent cation. This latter center is then the $Z_2$ center. Reasoning from the similarity in behavior of the F and F' bands to the $Z_2$ and $Z_3$ bands, he considers the $Z_3$ center to be a $Z_2$ center plus a second trapped electron.

Later Seitz (24, p. 136) proposed a different set of models. He considers the $Z_1$ center to be an electron captured by an unassociated divalent cation. The positive-ion vacancy, which remains from the impurity complex, and the negative-ion vacancy, which remains from the F center that was ionized, are thought to unite to form the vacancy pair, a mobile unit. Starting with the $Z_1$-center model, he proposes three mechanisms for the experimentally observed transformation of $Z_1$ centers to $Z_2$ centers:

1. The vacancy pair migrates to and associates with a $Z_1$ center.
2. The vacancy pair migrates to and associates with an impurity complex (perhaps even at a lower temperature); this new complex then captures the electron ionized thermally from
the $Z_1$ center and subsequently ejects a positive-ion vacancy.

3. An impurity complex migrates to and associates with an F center.

Thus the Seitz model for a $Z_2$ center is an electron trapped by a complex consisting of a divalent cation, a positive-ion vacancy, and a negative-ion vacancy. For the $Z_3$-center model Seitz agrees with Pick that it is a $Z_2$ center plus a second trapped electron. These $Z$-center models of Pick and Seitz are summarized diagrammatically in Figure 2.

Outline of later experiments

Camagni et al. (1; 2) have studied the conversion of the F band to the $Z_1$ band in considerable detail in strontium-doped potassium chloride crystals, with results generally confirming the earlier work of Pick. They emphasize two observations as being particularly striking:

1. No initial $Z_1$ band can be found in freshly colored crystals, regardless of whether coloration was done additively or by x-irradiation.

2. In an additively colored crystal the total conversion of the F band to the $Z_1$ band can be achieved only if the initial F band is sufficiently small.

A more thorough discussion of this second result, the saturation effect, leads them to conclude that only the unassociated strontium ions have an appreciable capture cross section for conduction.
Fig. 2.—Z-center models
electrons, but that most of the strontium ions in the crystal are associated with positive-ion vacancies.

Further investigations of strontium-doped potassium chloride crystals have been conducted by Chiarotti, Fumi, and Giulotto (4, p. 317-319) with the following results:

1. Crystals quenched from the coloring temperature to room temperature exhibit only the F band.
2. The Z₂ band also appears directly (primary Z₂ band) in crystals that are cooled slowly.
3. Prolonged heating in the dark at about 110°C enhances the primary Z₂ band, with a corresponding decrease in the F band.
4. The amount of secondary Z₂ band that can be formed by thermal destruction of the Z₁ band is strongly dependent on the rate at which the crystal was originally cooled from the coloring temperature.

The authors explain the formation of the primary Z₂ band and its enhancement by heating in the dark by the diffusion of impurity complexes to F centers, this combination being the Seitz model of a Z₂ center. The explanation of the fourth observation rests on the assumption that the Z₁ center is ionized thermally at 110 °C. The cooling rate is then supposed to determine the distribution of defect aggregates, in particular the complex consisting of an impurity complex associated with a vacancy pair, which, as was suggested by Seitz, can capture the electron and eject a positive-ion vacancy to
form the $Z_2$ center.

Cole and Friauf (6, p. 389-391) have recently observed a new band in strontium-doped potassium chloride, which they call the $Z_4$ band, whose outstanding characteristic is its appearance and disappearance in step with the $Z_1$ band. Accepting the Seitz proposals for the other three $Z$ centers, they suggest that the $Z_4$ center might be an electron trapped by an impurity complex.

Chiarotti, Fumi, and Giulotto (4, p. 319-320) subjected strontium-doped potassium chloride crystals containing $F$ and $Z_2$ centers to about 25% bleaching with polarized light lying in the $Z_2$ band. The absorption was then measured with light polarized both perpendicular and parallel to the bleaching light, but no dichroism was detected.

After exciting the $Z_2$ centers in strontium-doped potassium chloride crystals with polarized light, West and Compton (34, p. 577-578) observed that the emission is unpolarized. This result also implies that the $Z_2$ center has a high degree of symmetry.

Dichroism of the $Z_2$ band in strontium-doped sodium chloride was observed, however, by Remaut and Dekeyser (23). The crystals were bleached with light polarized in either of two directions and the absorption was then measured successively with light polarized in both these directions. The decrease in absorption was greatest when measured with light polarized in the same direction as the bleaching light. When the crystals were stored in the dark for at least five hours after bleaching and then subjected to absorption
measurements, no dichroism was observed. These authors think that further work is needed before definite conclusions can be made.

The electron spin resonance of $Z_1$ centers in calcium-doped and strontium-doped potassium chloride crystals has been investigated by Kawamura and Ishiwatari (14); they conclude that their results may favor the Seitz model of the $Z_1$ center.

In Table 1 are collected experimental results for the positions of the various $Z$ bands.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Band</th>
<th>Energy (eV)</th>
<th>Temperature</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl:Ca</td>
<td>$Z_1$</td>
<td>2.10</td>
<td>-215°C</td>
<td>21, p. 76</td>
</tr>
<tr>
<td></td>
<td>$Z_2$</td>
<td>2.03</td>
<td>-215°C</td>
<td>21, p. 76</td>
</tr>
<tr>
<td>KCl:Sr</td>
<td>$Z_1$</td>
<td>2.06</td>
<td>80°K</td>
<td>1, p. 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.00</td>
<td>293°K</td>
<td>1, p. 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.08</td>
<td>-215°C</td>
<td>21, p. 76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.10</td>
<td>77°K</td>
<td>33, p. 155</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.10</td>
<td>77°K</td>
<td>34, p. 578</td>
</tr>
<tr>
<td></td>
<td>$Z_2$</td>
<td>1.95</td>
<td>-215°C</td>
<td>21, p. 76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.97</td>
<td>77°K</td>
<td>33, p. 155</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.94</td>
<td>77°K</td>
<td>34, p. 578</td>
</tr>
<tr>
<td></td>
<td>$Z_4$</td>
<td>1.44</td>
<td>100°K</td>
<td>6, p. 389</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.46</td>
<td>77°K</td>
<td>33, p. 155</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.44</td>
<td>77°K</td>
<td>34, p. 578</td>
</tr>
<tr>
<td>KCl:Ba</td>
<td>$Z_1$</td>
<td>2.07</td>
<td>-215°C</td>
<td>21, p. 76</td>
</tr>
<tr>
<td></td>
<td>$Z_2$</td>
<td>1.91</td>
<td>-215°C</td>
<td>21, p. 76</td>
</tr>
<tr>
<td>NaCl:Sr</td>
<td>$Z_1$</td>
<td>2.45</td>
<td>-207°C</td>
<td>22, p. 129</td>
</tr>
<tr>
<td></td>
<td>$Z_2$</td>
<td>2.42</td>
<td>-203°C</td>
<td>22, p. 129</td>
</tr>
</tbody>
</table>
Objective and Scope of the Present Work

Since some of the experimental results just cited support the Pick models while others support the Seitz models, it is of interest to attempt the prediction of the optical transition energies for the various models. Ideally, the results of such theoretical calculations could be used to choose the better of the two sets of models. No accounts of such calculations for alkali halides doped with alkaline earth halides have yet been published. The primary objective of this work is to undertake such calculations.

All the models proposed to account for the different Z bands consist of an alkaline earth cation with or without associated vacancies at which one or two electrons have been trapped. The simplest of these, the unassociated cation with one trapped electron, is the basis of all the work to be described. It will be noticed that this center is the Z₂ model of Pick and the Z₁ model of Seitz. Thus, if the theoretical results agree closely with the experimental positions of one of these bands, added support will accrue to the corresponding set of models.

The problem is treated as a one-electron problem and thus reduces to the solution of the Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + V\right)\psi = \omega_0 \psi.$$  

This equation, as are all others in this paper unless noted otherwise, is written in Hartree atomic units. Thus the unit of energy is twice the ionization energy of the hydrogen atom, the unit of mass is the
electron mass, and the unit of length is the first Bohr radius of the hydrogen atom. The solution of this equation is estimated by the variation method. A suitable one-parameter trial function is chosen and substituted into the equation

$$ W = \int \psi (-\frac{1}{2} \nabla^2 + V) \psi \, d\tau $$

to obtain the energy as a function of the variation parameter. The energy is then minimized with respect to this parameter. In general the more closely the trial wave function approximates the true wave function of the system, the more closely will the energy estimated from the variation method approximate the true energy. The great utility of this method arises in that even a poor trial function often leads to a reasonably good energy estimate. In the problem at hand, as Mott and Gurney (20, p. 85) have pointed out, the field in which the electron moves, and hence its potential energy, $V$, depends on its wave function; thus the energy must be determined by a self-consistent method. This is precisely the approach chosen by Simpson (28) for his calculations of the F-center energy levels.

A number of other theoretical studies of the F center— for details the interested reader is referred to the excellent review article by Gourary and Adrian (10)—have been made, including some published after this work was begun. The approach of Simpson is used here because of its relative simplicity and because of its success in the prediction of F-band energies, especially in the
studies by Smith (29, p. 73-105; 30).

Throughout the discussion the host lattice is considered to be a continuous dielectric medium with static dielectric constant $k$ and optical dielectric constant $k_0$. The different treatments arise mainly through differences in two factors: the charge distribution of the impurity cation and the potential energy of the impurity-cation site. The magnitudes of the various physical constants used in the computations are listed in Appendix I.
II. PRELIMINARY CALCULATIONS

Interstitial Point Charge

Expression for the field

Although there is little likelihood that the impurity cation occupies an interstitial position in the alkali halide host lattice, at least one significant advantage will result from a somewhat detailed consideration of this case: the application of the self-consistent variational procedure will be seen for a particularly simple calculation. The impurity will be treated as a point charge placed in a continuous dielectric medium with no elastic distortion of the medium.

With a cation of charge Q present interstitially, and in the absence of the electron, a static field of magnitude $Q/r^2k$ exists throughout the crystal. With the electron bound to this cation, however, the resultant field is considerably modified. If, for a moment, the electron is thought to occupy an orbit a few lattice constants distant from the cation, the field can be calculated at two extreme points: at very large distances the electron will appear to have neutralized one unit of charge of the cation, and the field will be $(Q-1)/r^2k$; at very small distances, inside the electron's orbit, the ions will be unable to follow the electron's motion, and consequently the field will still be $Q/r^2k$.

In actuality, of course, the electron is not confined to any one orbit but has a certain probability of being at any specified
distance from the cation. Thus, when the electron momentarily is
far from the cation, it still experiences the field \((Q-1)/r^{2k}\), but
in addition it will be attracted by the unit of charge it no longer
neutralizes. Since the electron will sweep out to a large distance
for only an instant, the ions will be unable to follow the motion,
and the added contribution to the field will have the form \(1/r^{2k_0}\).
At very small distances the field will still be given by \(Q/r^{2k}\).
But at intermediate distances the field will have a value between
those given at these two extreme points.

Evidently then, the field experienced by the electron depends
on its own probability distribution. The actual field, \(E\), at
distance \(r\) from the impurity cation can be estimated as follows:
the limiting field for small distances contributes to \(E\) an amount
proportional to the probability that the electron is beyond \(r\), and,
similarly, the limiting field for large distances contributes to \(E\)
an amount proportional to the probability that the electron is within
\(r\). If the probability that the electron is in a sphere of radius \(r\)
about the cation is denoted by \(p\), then the field is

\[
E \cdot p \left( \frac{Q}{r^2 K} + \frac{1}{r^2 K_0} \right) + (1-p) \frac{Q}{r^2 K} = \frac{Q}{r^2 K} + \frac{c \rho}{r^2}, \quad \text{where } c = \left( \frac{1}{K_0} \right).
\]

From its definition

\[
p = \int_0^r \rho^2 d\tau.
\]

Since \(p\) approaches zero as \(r\) becomes very small and approaches unity
as \(r\) becomes infinite, \(E\), as calculated from this equation, becomes
\(Q/r^{2k}\) at small \(r\) and \((Q-1)/r^{2k} + 1/r^{2k_0}\) at large \(r\); thus the derived
equation gives the required results for these extreme points.

Derivation of equations and results

Before $p$ can be calculated, an estimate of $\psi$ must be made. For $Q = 1$ the field at small $r$ is $1/r^2k$, and at large $r$, $1/r^2k_0$. Except for the presence of the effective dielectric constant in the denominator, this problem is identical to the hydrogen atom problem. Although the field expressions are more complicated for larger values of $Q$, sufficient similarity to the hydrogen atom problem remains to make the use of hydrogen-like wave functions a reasonable approximation. For the ground state, therefore, $\psi$ will be approximated by the ls hydrogen-like wave function. Then

$$\psi_1 = \left(\frac{n^2}{\pi}\right)^{1/2} e^{-\mu r},$$

$\rho = 1 - (2\mu^2 r^2 + 2\mu r + 1) e^{-2\mu r},$

and

$$E = \frac{\rho}{r^2 k} + \frac{c}{r^2} \left\{ 1 - (2\mu^2 r^2 + 2\mu r + 1) e^{-2\mu r} \right\}.$$

The potential energy of the electron is calculated from the field as follows:

$$V = \int_{\infty}^{r} E \, d\rho = -\frac{1}{r} \left( \frac{Q-1}{k} + \frac{1}{k_0} \right) + \frac{c}{r} (\mu r + 1) e^{-2\mu r}.$$

As trial function is chosen

$$\psi_2 = \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\lambda r}.$$
from which is computed the energy

\[ W_3 = \int \psi_2 \left( -\frac{1}{2} \nabla^2 + V \right) \psi_2 \, d\tau \]

\[ = \frac{\lambda^2}{2} - \lambda \left( \frac{\theta - 1}{K} + \frac{\lambda^3}{(\lambda + \mu)^3} \right) \left( 1 + \frac{\mu}{\lambda + \mu} \right). \]

Minimization of \( W \) with respect to the variation parameter \( \lambda \) is achieved by setting

\[ \frac{\partial W}{\partial \lambda} = 0, \]

and the self-consistency requirement is satisfied by setting \( \psi_1 = \psi_2 \), which demands that \( \lambda = \mu \). This gives

\[ \lambda = \frac{\mu}{16} \left\{ \frac{(16 \theta - 5) K_0 + 5K}{K_0 K} \right\} = \frac{5\gamma}{16} + \frac{\theta}{K} \]

and

\[ W_g = -\frac{\lambda^2}{2} - \frac{5\lambda\gamma}{16}. \]

The energy expression for the excited state is found in exactly the same way, except that a 2p hydrogen-like wave function is used. The derivation is outlined below. The equations are given in exactly the same order as those for the ground state, and they are derived by the same procedures.

\[ \psi_1 = \left( \frac{\lambda^5}{\pi} \right)^{1/2} \gamma \cos \phi \ e^{-\lambda \gamma r}, \]

\[ \rho = 1 - \left( \frac{2}{3} \lambda^4 r^4 + \frac{4}{3} \lambda^3 r^3 + 2 \lambda^2 r^2 + 2 \lambda r + 1 \right) e^{-2\lambda r}, \]

\[ E = \frac{\theta}{K^2} + \frac{\gamma}{r^2} \left\{ 1 - \left( \frac{2}{3} \lambda^4 r^4 + \frac{4}{3} \lambda^3 r^3 + 2 \lambda^2 r^2 + 2 \lambda r + 1 \right) e^{-2\lambda r} \right\}. \]
\[ \psi = -\frac{1}{r} \left( \frac{\frac{Q - 1}{r} + \frac{1}{K_0}}{1} + \frac{e}{r} \left( \frac{\frac{1}{3} a^2 r^2 + a^2 r^2 + \frac{3}{2} d r + 1}{2} \right) e^{-2a r} \right) \]

\[ \psi_2 = \left( \frac{e}{r} \right)^{1/2} \psi \cos \theta e^{-2a r}, \]

\[ W_k = \frac{e^2}{2} - \frac{\beta^2}{2} \left( \frac{Q - 1}{r} + \frac{1}{K_0} \right) + \frac{\beta^2}{2} \left( \frac{\beta + a}{2} \right) \left( 1 + \frac{3}{\beta + a} + \frac{\beta^2}{(\beta + a)^2} + \frac{\beta^3}{(\beta + a)^3} \right) \]

\[ \frac{dW_k}{d\beta} = \alpha, \quad \psi_1 = \psi_2, \quad \text{and} \quad \beta = \alpha. \]

\[ \beta = \frac{1}{512} \left( \frac{(256 \Phi - 93) K_0 + 93 K}{K_0 K} \right) = \frac{93 \Phi}{512} + \frac{\Phi}{2K} \]

and \[ W_k = -\frac{\beta^2}{2} - \frac{93 \beta e}{512}. \]

The results of these calculations for a divalent impurity cation are given in Table 2.

**TABLE 2**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( W_g ) (ev)</th>
<th>( W_e ) (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>-4.434</td>
<td>-1.203</td>
</tr>
<tr>
<td>NaCl</td>
<td>-3.465</td>
<td>-0.957</td>
</tr>
</tbody>
</table>

Optical transition energy

As Gourary and Adrian (10, p. 160-161) have pointed out,
the difference between the ground and excited state energies as computed here can not be compared directly with the experimentally determined energy of the optical absorption. The reason for this can be seen by comparing the equations for the field in the two states. The second term, $Q/r^2k$, is the same in both equations; the first term, $pc/r^2$, changes, however, because $p$ varies from one state to the other. The quantity $c$ is determined by the part of the static dielectric constant that depends on ionic displacements only and not on deformation of the electron clouds. The quantity $p$ depends on the probability distribution of the trapped electron. In other words the first term reflects the contribution to the field from the ionic displacements, which are determined by the time-average distribution of the trapped electron and remain fixed as the electron moves. Immediately after excitation of the electron has occurred, $p$ is determined by the excited-state probability distribution of the trapped electron. But the optical absorption act is finished before the ions have time to move to the new positions dictated by the changed probability distribution of the trapped electron. During the absorption act, therefore, the electron's potential energy remains that of the ground state; it is only after the optical transition is completed that the excited state potential energy applies.

The excited state energy immediately after the optical transition, then, must be calculated by using $V$ from the ground state determination in conjunction with the excited state trial
wave function. The results of this procedure are

$$\beta - \frac{1}{2} \left( \frac{Q-1}{K} + \frac{1}{K_0} \right) + \frac{c \beta^4}{(\beta + \mu)^4} \left\{ \frac{5}{2} + \frac{5 \mu - 2 \beta}{\beta + \mu} - \frac{5 \beta \mu}{(\beta + \mu)^2} \right\} = 0$$

and

$$W_{ag} = \frac{\beta}{2} \left\{ \beta - \left( \frac{Q-1}{K} + \frac{1}{K_0} \right) + \frac{c \beta^4}{(\beta + \mu)^4} \left( 1 + \frac{2 \mu}{\beta + \mu} \right) \right\}.$$

Evaluation of these equations for $Q = 2$ gives the results of Table 3.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$W_g$ (ev)</th>
<th>$W_{eg}$ (ev)</th>
<th>$\Delta W$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KC1</td>
<td>-4.434</td>
<td>-1.487</td>
<td>2.947</td>
</tr>
<tr>
<td>NaCl</td>
<td>-3.465</td>
<td>-1.218</td>
<td>2.247</td>
</tr>
</tbody>
</table>

These results can be compared with the experimental $Z_1$- and $Z_2$-band energies given in Table 1—about 1.9 to 2.1 ev for potassium chloride and 2.4 to 2.5 ev for sodium chloride.

Substitutional Point Charge

Comparison with interstitial point charge

Although the derivations of the preceding section have been carried out for interstitial point ions of charge $Q$, they may also be considered roughly applicable to substitutional point ions of charge $Q + 1$. An estimate of the optical transition energy of an
electron trapped by a substitutional divalent cation is obtained, then, by setting \( Q = 1 \) in the equations derived for the interstitial point charge. The results, 1.047 ev in potassium chloride and 0.840 ev in sodium chloride, are much lower than the experimental values cited earlier and make it evident that a more detailed analysis is necessary.

With the impurity present substitutionally instead of interstitially the problem is altered in two important respects. First, since the impurity ion occupies a site normally filled by a monopositive ion, its effective charge is one less than its actual charge, that is \( Q - 1 \); and second, the ion in question no longer is placed at a site of zero potential (in the perfect lattice), so the actual potential at the lattice point must be estimated.

This problem is treated by assuming that a host cation is removed from the lattice, leaving a spherical cavity in the dielectric continuum. The impurity is then placed in this cavity and is considered to be a point charge at its center. The radius of the cavity, \( R \), is assumed equal to the radius of the impurity ion.

The electron's potential energy is determined by two separate methods, depending on whether the electron is inside or outside the cavity. No attempt has been made to make \( V \) continuous at \( r = R \), the point of transition between the two cases. When the electron is outside the cavity, it experiences a field of the same form as was derived in the interstitial ion problem, except that the actual ionic charge must be reduced by one to get the effective charge. Thus the
Field is

\[ E = \frac{Q - 1}{r^2 K} + \frac{e \cdot p}{r^2}. \]

Field inside the cavity

Inside the cavity the electron experiences a field arising from two sources—the ions and dipoles surrounding the cavity, and the impurity cation itself. The field of the ions and dipoles at the vacant lattice point is made up of the field from the otherwise perfect lattice, plus that from the lattice polarization. The contribution to the electron's potential energy from the former field is just the Madelung potential energy, \( \alpha/a_0 \), where \( \alpha \) is the Madelung constant and \( a_0 \) the interionic spacing; that from the latter field is known as the Jost potential energy (13, p. 470).

Various investigators attempting to calculate the F-center energy levels have cast the Jost potential energy expression in different forms. Krumhansl and Schwartz (18) have investigated this question quite thoroughly, but a detailed account of their work did not appear until recently (10, p. 195-196). In a later section of this paper their arguments will be followed in deriving the correct expression for the Jost potential energy. The calculations of this section, however, which were carried out with the incorrect expression

\[ V_o = \frac{1}{R} \left( 1 - \frac{1}{K_0} \right), \]

the one used by Simpson, will be discussed as they stand. Thus the total contribution of the ions and dipoles to the electron's
potential energy is

\[ V_I = \frac{\alpha}{a_o} + \frac{1}{R} (1 - \frac{1}{K_o}) . \]

With the impurity cation taken as a point charge, some account must be made of its polarizability; that is, it must be considered a point charge \( Q \) imbedded in a dielectric with some effective optical dielectric constant that takes into account the polarization of the electron cloud surrounding the nucleus. This is done by taking the high-frequency dielectric constant of the host crystal and adjusting it for the difference in polarizabilities of the host and impurity cations. By way of clarification it should be pointed out that the effective charge of the impurity acting on the electron when it is within the cavity is certainly its actual charge. This part of \( V \) will therefore depend on \( Q \), not on \( Q - 1 \). The electron's potential energy in the field of the impurity is, then,

\[ V_2 = -\frac{Q}{r K_{eff}} . \]

Calculation of the effective dielectric constant

The expression

\[ K_o = 1 + \frac{4\pi N\alpha_1}{1 - \frac{4}{3} \pi N\alpha_1} + \frac{4\pi N\alpha_2}{1 - \frac{4}{3} \pi N\alpha_2} \]

given by Mott and Gurney (20, p. 18), reproduces the experimental values of \( k_o \) for the alkali halides quite well. \( \alpha_1 \) and \( \alpha_2 \) are the polarizabilities of anion and cation, respectively, and \( N \) is the number of ion pairs per unit volume. The equation can be rewritten
in a more useful form by dividing the numerator and denominator of each fraction by $N$. The reciprocal of $N$ is, of course, the volume per ion pair, $V_m$:

$$k_0 = 1 + \frac{4\pi \alpha_1}{V_m - \frac{4}{3}\pi \alpha_1} + \frac{4\pi \alpha_2}{V_m - \frac{4}{3}\pi \alpha_2}.$$ 

The high-frequency dielectric constant of the host lattice, $k_0$, is a property of the crystal as a whole, but it depends on a property of the individual ions—their polarizability. The use of $k_0$ inside the cavity containing the impurity cation is not correct because this cation has a polarizability differing from that of the host cation it replaces. The environment of the impurity cation is the same as that of a host cation in the perfect crystal. If the lattice polarization and the difference in cation size are ignored, the change in dielectric constant depends only on the change in cation polarizability. The dielectric constant, $k_{\text{eff}}$, effective in the vicinity of the cavity, can then be estimated from $k_0$ by replacing the host-cation polarizability with the impurity-cation polarizability.

It is assumed that the anion polarizability contributes the same amount to both $k_0$ and $k_{\text{eff}}$, so the first two terms on the right-hand side of the last equation can be replaced by a constant, $c_1$. Thus,

$$k_0 = c_1 + \frac{4\pi \alpha_2}{V_m - \frac{4}{3}\pi \alpha_2},$$

and

$$k_{\text{eff}} = c_1 + \frac{4\pi \alpha_2}{V_m - \frac{4}{3}\pi \alpha_2}.$$
where $C_2$ is the ratio of the impurity-cation polarizability to the host-cation polarizability. By subtraction of the first equation from the second, an expression for $k_{\text{eff}}$ is obtained.

$$k_{\text{eff}} = \frac{1}{4\pi} \frac{d^2}{d^2 x} \left( \frac{C_2}{V_m - \frac{4\pi C_2 d^2}{3}} - \frac{1}{V_m - \frac{4\pi d^2}{3}} \right).$$

Values of the effective dielectric constant calculated from this equation are given in Table 4.

**TABLE 4**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$k_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl:Ca</td>
<td>2.05</td>
</tr>
<tr>
<td>KCl:Sr</td>
<td>2.14</td>
</tr>
<tr>
<td>NaCl:Ca</td>
<td>2.34</td>
</tr>
<tr>
<td>NaCl:Sr</td>
<td>2.46</td>
</tr>
</tbody>
</table>

**Derivation of equations and results**

From here on the derivations are carried out exactly as in the problem of the interstitial impurity with the use of the same trial wave functions. Pertinent equations are given below:

**Ground state:**

$$\mathcal{V} = \frac{\alpha}{a_o} + \frac{1}{R} (1 - \frac{1}{K_0}) - \frac{Q}{r K_{\text{eff}}},$$

$$\mathcal{V} = V_0 - \frac{Q}{r K_{\text{eff}}}, \quad \sigma \leq r \leq R,$$

$$\mathcal{V} = -\frac{Q - 2}{r \lambda} - \frac{1}{r K_0} + \frac{c}{r} (\mu r + 1) e^{-2\mu r}, \quad R \leq r \leq \infty.$$
\[
\lambda - \frac{Q}{K_{\text{eff}}} + c \left( 2\lambda^2 R^3 + \frac{1}{2} \lambda^2 R^2 - \frac{11}{4} \lambda R - \frac{11}{16} \right) e^{-4\lambda R} \\
+ \left\{ 4 V_0 \lambda^2 R^3 - \left( \frac{Q}{K_{\text{eff}}} - \frac{1}{K} - \frac{Q-2}{K} \right) (4\lambda^2 R^2 - 2\lambda R - 1)^2 e^{-2\lambda R} = 0, \right. \\

W_g = \frac{\lambda^2}{2} + V_0 + \frac{c \lambda}{K} \left( \lambda R^2 + \frac{3}{2} \lambda R + \frac{3}{8} \right) e^{-4\lambda R} - \frac{Q\lambda}{K_{\text{eff}}} \\
+ \left\{ \left( \frac{Q}{K_{\text{eff}}} - \frac{1}{K} - \frac{Q-2}{K} \right) \lambda (2\lambda R + 1) - V_0 (2\lambda^2 R^2 + 2\lambda R + 1)^2 e^{-2\lambda R}. \right. \\

\text{Excited state;} \\
V = \frac{\lambda}{Q} + \frac{1}{R} \left( 1 - \frac{1}{K_0} \right) - \frac{Q}{r K_{\text{eff}}} \\
= V_0 - \frac{Q}{r K_{\text{eff}}}, \quad 0 \leq r \leq R, \\

V = -\frac{Q-2}{r K} - \frac{1}{r K_0} + \frac{c}{r} \left( \frac{1}{3} \lambda^2 R^3 + \lambda^2 R + \frac{3}{2} \lambda R + 1 \right) e^{-2\lambda R}, \\
\quad R \leq r \leq \infty, \\

\beta = \frac{Q}{2K_{\text{eff}}} + \left\{ \frac{4}{3} V_0 \beta^2 R^5 - \left( \frac{Q}{K_{\text{eff}}} - \frac{1}{K_0} - \frac{Q-2}{K} \right) \left( \frac{4}{3} \beta^4 R^4 \right. \\
- \frac{2}{3} \beta^2 R^2 - \beta R - \frac{1}{2} \right) e^{-2\beta R} + \left( \frac{2}{9} \beta^6 R^6 - \frac{1}{2} \beta^6 R^6 \right. \\
\left. - \frac{1}{12} \beta R^5 + \frac{63}{48} \beta^4 R^4 + \frac{163}{48} \beta^3 R^3 + \frac{163}{64} \beta^2 R^2 \\
+ \frac{163}{128} \beta R + \frac{163}{512} \right\} e^{-4\beta R} = 0, \]
\[ W_0 = \frac{\beta^2}{2} + V_0 - \frac{Q^2}{2K_{aff}} + \left\{ \left( \frac{Q}{K_{eff}} - \frac{1}{K_{o}} - \frac{Q^2}{K} \right) \beta \left( 4p^3R^3 \ight.ight. \\
+ 6p^2R^2 + 6pR + 3 \right) - \frac{V_0}{3} \left( 2\beta^4R^4 + 4p^3R^3 + 6p^2R^2 \
+ 6pR + 3 \right) \} e^{-2\beta R} \\
+ \frac{Q^2}{18} \left( 2\beta^6R^6 + 9\beta^5R^5 + \frac{81}{4}\beta^4R^4 + \frac{105}{4}\beta^3R^3 \\
+ \frac{315}{16}\beta^2R^2 + \frac{315}{32}\beta R + \frac{315}{128} \right) e^{-4\beta R}. \]

As was mentioned in conjunction with the interstitial-impurity computations, the estimation of the energy of the optical absorption demands the use of the ground state potential energy with the excited state wave function. A comparison of \( V \) in the ground state with that in the excited state, however, shows that they differ, and then only slightly, in the region outside the cavity. Since both \( |V| \) and \( \psi \) are relatively small in this region, it does not seem likely that the use of the excited state potential energy, that is, the electron's potential energy after the polarization of the lattice has adjusted to the new charge distribution, will contribute any substantial error to the calculation. Consequently, the energy of the optical transition is taken as the difference between the two equilibrium energy levels. Any appreciable error that is introduced will make the excited state energy slightly too high. These equations have been enumerated for several cases, the results being given in Table 5.
TABLE 5
ENERGY LEVELS OF SUBSTITUTIONAL CATIONS

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( W_g ) (ev)</th>
<th>( W_e ) (ev)</th>
<th>( \Delta W ) (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl:Ca</td>
<td>-2.10</td>
<td>-0.51</td>
<td>1.59</td>
</tr>
<tr>
<td>KCl:Sr</td>
<td>-1.69</td>
<td>-0.51</td>
<td>1.18</td>
</tr>
<tr>
<td>NaCl:Ca</td>
<td>-1.36</td>
<td>-0.43</td>
<td>0.93</td>
</tr>
<tr>
<td>NaCl:Sr</td>
<td>-1.08</td>
<td>-0.43</td>
<td>0.65</td>
</tr>
</tbody>
</table>

It is not surprising to see such poor agreement with the experimental results cited previously, since the model is a naive one. It is interesting to note, however, that the excited state energies depend primarily on the identity of the host lattice and not on the particular impurity. Evidently, the main source of error lies in the inadequate description of the electron's potential energy in the ground state in the region near the impurity cation, that is, inside the cavity.

Substitutional Distributed Charge

An artificial potential energy function

The simplest method of describing the electronic charge distribution about the impurity-cation nucleus is the statistical procedure of Thomas and Fermi. An artificial potential energy function with some of the characteristics of the Thomas-Fermi potential energy is used in this section to lay the foundations for the later use of the Thomas-Fermi method itself. These
preliminary remarks concern the free cation; its interaction with
the crystal is considered later.

The cation is taken to have nuclear charge Z and ionic charge
Q, where Q does not include the charge of the one valence, or trapped,
electron. The effect of this last electron on the potential distrib-
ution is ignored. In Ca\textsuperscript{+}, for example, Z = 20, Q = 2, and the
influence of the one remaining electron on the field of the nucleus
and the other 18 electrons is not considered. Thus, the potential
distribution, \( \phi(r) \), is determined by the nucleus and 18 electrons;
the potential energy of the valence electron is then \(-\phi(r)\). This
use of Q, therefore, is still consistent with its earlier meaning,
the charge of the ion before the electron is trapped.

The artificial potential energy function must be constructed
so that it satisfies the following boundary conditions:
1. As \( r \), the distance of the valence electron from the nucleus,
approaches zero, \( V \) approaches \(-Z/r\).
2. Outward from the ion boundary, at distance \( R \) from the nucleus,
\( V \) equals \(-Q/r\). Thus \( V \) must equal \(-Q/R \) at the ion boundary.
A function which satisfies these conditions and exhibits the general
form of the Thomas-Fermi potential energy is
\[
V = -\frac{Z}{r}e^{-aY} + \frac{Q}{R}e^{-aR} - \frac{a}{R} - \phi(r), \quad 0 \leq r \leq R,
\]
where \( a \) is an arbitrary constant.

That part of \( V \) arising from the Coulombic attraction of the
nucleus for the valence electron is \(-Z/r\). The potential energy
arising through interaction of the valence and core electrons is then found by difference to be

\[ V_{l\ell} = -\frac{Z}{r} e^{-ar} + \frac{Z}{r} + \frac{Z}{R} e^{-aR} - \frac{Q}{R}. \]

Through application of Poisson's equation to the potential of the core electrons, the core-electron charge density is found to be

\[ \rho = -\frac{1}{4\pi} \nabla^2 \Phi_{l\ell} = -\frac{Ze^2}{4\pi r} e^{-ar}. \]

Since the total electronic charge contained in the ion core is \(- (Z-Q) = -N\), integration of the charge density over the volume occupied by the core electrons gives a quantity which must equal \(-N\). This results in a relationship for fixing the value of the arbitrary constant \(\alpha\).

\[ \int_0^R \rho d\tau = -N, \text{ and} \]

\[ (aR+1) e^{-aR} = \frac{Q}{Z}. \]

Cation in vacuum

The degree of validity of this potential energy function can be estimated by using it to calculate the energy-level (in vacuum) values of a cation for which the experimental results are available. Ca\(^+\) was selected for this purpose. The requirement of orthogonality among the wave functions of core and valence electrons is satisfied by choosing 4s and 4p hydrogen-like wave functions for the trial functions of the ground and excited states, respectively.
The potential energy, as just derived, is

$$V = -\frac{Z}{Y} e^{-aY} - V_0, \quad 0 \leq Y \leq R,$$

$$V = -\frac{Q}{R}, \quad R \leq Y \leq \infty.$$

The solution is now obtained by the same variational procedure used before. No equations are listed here, since they are simpler versions of those appearing later when the Thomas–Fermi potential energy is used. Suffice it to say now that the results of this calculation for Ca\(^{+}\) in vacuum are \(-17.25\) ev for the ground state and \(-7.93\) ev for the excited state. Grotrian (11, p. 30) cites the corresponding experimental results as \(-11.37\) ev and \(-8.73\) ev, respectively. Although the calculated ground state lies nearly 50% too low, some worthwhile results are obtained by using this potential energy function.

Cation in a crystal

The next point of interest is the magnitude of the energy-level rise when the Ca\(^{+}\) ion is placed in a crystal. In essence this is the same problem as the substitutional point charge discussed
previously, except that now the cation is considered to be a charge distribution. Since the derivation is very laborious, only the ground state, again represented by a 4s trial wave function, is treated.

The field outside the cavity is still represented by the same equation that was used with the substitutional point charge, but, since a different trial wave function is being used, \( p \), and consequently \( V \), take different forms.

\[
\phi = 1 - \left( \frac{2}{q} \mu^2 \gamma^2 - \frac{7}{q} \mu^2 \gamma^7 + \frac{5}{4} \mu^2 \gamma^6 - 8 \mu^5 \gamma^5 + 6 \mu^4 \gamma^4 
+ 2 \mu^2 \gamma^2 + 2 \mu \gamma + 1 \right) e^{-2 \mu \gamma},
\]

\[
V = - \frac{Q}{Y K} - \frac{1}{Y K_0} + \frac{e}{Y} \left( \frac{1}{q} \mu^2 \gamma^7 - \frac{5}{4} \mu^2 \gamma^6 + \frac{3}{2} \mu^5 \gamma^5 - \mu^4 \gamma^4 
+ \frac{3}{2} \mu^3 \gamma^3 + \frac{3}{2} \mu^2 \gamma^2 + \frac{7}{4} \mu \gamma + 1 \right) e^{-2 \mu \gamma}.
\]

Inside the cavity the potential energy is

\[
V = \frac{\alpha}{a_0} + \frac{1}{R} \left( 1 - \frac{1}{K_0} \right) - \frac{\pi}{Y} e^{-a \gamma} + \frac{\pi}{R} e^{-a R} - \frac{Q}{R}.
\]

The Simpson formulation of the Jost potential energy is used here also.

Computations for \( Ca^+ \) in potassium chloride result in a ground state value of -6.43 ev; the calculated ground state has been raised 10.82 ev by placing the ion in the crystal.

Empirical correction term

A somewhat more significant result is obtained, however, if
a correction term is added to the potential energy function and
adjusted to bring the result of the vacuum calculation into coinci-
dence with the experimental value. A term of the form $A/r$ can be
added without changing the electronic charge density calculated from
Poisson's equation; thus the constant $a$ does not need re-evaluation.
The second boundary condition demands that the term $-A/R$ be added
concomitantly. Thus

$$V = -\frac{Z}{r}e^{-a r} + \frac{A}{r} + \frac{Z}{R} e^{-a R} - \frac{A}{R} - \frac{Q}{R}$$

$$= -\frac{Z}{r}e^{-a r} + \frac{A}{r} - V_0 , \quad 0 \leq r \leq R,$$

$$V = -\frac{Q}{R} , \quad R \leq r \leq \infty .$$

Using this $A$-dependent expression for $V$ in the variational procedure
gives rise to $A$-dependent terms in the expressions for $W$ and its
derivative; denote these correction terms by $W_c$ and $W_c'$, respec-
tively. As can be seen above, $V_0$ also depends on $A$.

It is desired to enumerate $A$ so that the energy-level value
calculated for the ground state of Ca$^+$ in vacuum coincides with the
empirical value. To achieve this, proceed as follows:

1. With $A$ equal to zero, calculate $W$ from the minimizing value
of $\lambda$. This is precisely what was done in the original
calculation of the vacuum ground state, the resulting $W$ being
equal to $-17.25$ ev.

2. Find the difference between this calculated value of $W$ and
the experimental one, equate it to $W_c$, and solve for $A$.

3. With $A$ no longer equal to zero, the value of $V_0$ will change, and its new magnitude must be determined.

4. Using this new value of $V_0$, set $W'$, including $W_c'$ this time, equal to zero and again solve for $A$.

5. Using this new value of $A$, solve for the new value of $W$, this time including $W_c$ in the energy expression.

6. Again equate the difference between calculated and experimental energies to $W_c$ and solve for $A$.

7. Use this new estimate of $A$ in step 3, and continue repeating steps 3 through 6 until two successive estimates of $A$ differ insignificantly from one another.

The resulting value of $A$ is 2.346.

Now the ground state energy for Ca$^+$ in potassium chloride is recalculated with the terms $+2.346/r$ and $-2.346/R$ added to the expression for $V$. The resultant energy is $-3.26$ ev. Thus, addition of the correction term, evaluated to raise the energy level 5.38 ev in vacuum, raises the energy 3.17 ev in the crystal. The difference between the ground states in vacuum and in the crystal is now 8.61 ev, a decrease of 2.21 ev compared with the uncorrected calculations.

Approximation of the field outside the cavity

A great deal of the labor of these derivations revolves around the use of $p$ in the expression for the field outside the cavity—so much, in fact, that it is desirable to give attention to
possible approximations for this expression. The equation for the field outside the cavity is reproduced below for convenience.

\[ E = \frac{Q-1}{r^2 K} + \frac{c \cdot R}{r^2}. \]

When \( r \) is near \( R \) in magnitude, \( p \) is small, and the field approaches \((Q-1)/r^2k\). On the other hand, for very large \( r \), \( p \) approaches unity, and the field becomes \( Q-2/r^2k + 1/r^2k_0 \).

A function which exhibits the same limiting behavior is

\[ \frac{1}{r^2} \left( \frac{Q-2}{K} + \frac{1}{k_0} \right) - \frac{c \cdot R}{r^3}. \]

If the original field equation is replaced by this approximation expression, the derivations can be carried out very easily. Furthermore, the ground state energy for \( \text{Ca}^+ \) in potassium chloride, using this approximation, is \(-3.32 \text{ ev}\), only 0.06 ev lower than that obtained from the self-consistent procedure.

In the self-consistent procedure the electron’s potential energy, as indicated earlier, is

\[ V = -\frac{Q-2}{VK} - \frac{1}{VK_0} + \frac{c}{k} \left( \frac{1}{3} \mu_7^2 r^7 - \frac{5}{9} \mu_6^2 r^7 + \frac{3}{2} \mu_5^2 r^5 r^4 \right) \]

\[ + \frac{3}{2} \mu_3^2 r^3 + \frac{3}{2} \mu_2^2 r^2 + \frac{7}{4} \mu r + 1 \right) \Delta^{-2} \mu r. \]

On the basis of the above approximation function the electron’s potential energy is

\[ V = -\frac{Q-2}{VK} - \frac{1}{VK_0} + \frac{c \cdot R}{r^2}. \]
These two expressions for $V$ can be compared by comparing $R/2r$ with

$$
\left( \frac{1}{q} \mu^7 r^7 - \frac{5}{q} \mu^6 r^6 + \frac{3}{2} \mu^5 r^5 - \mu^4 r^4 + \frac{3}{2} \mu^3 r^3 + \frac{3}{2} \mu^2 r^2 + \frac{7}{4} \mu r + 1 \right) e^{-2\mu r}.
$$

When this is done, it is found, that, throughout a substantial range, the latter quantity is roughly twice the former. This suggests that the factor $1/2$ in the second term of the approximation function for $V$ should be omitted. Repeating the calculations with this second approximation for $V$ gives a value of $-3.16$ ev for the ground state of Ca$^+$ in KCl, 0.10 ev higher than the result of the self-consistent method.

Conclusions

The energy of the excited state of Ca$^+$ in potassium chloride, obtained by using the 4p hydrogen-like wave function in the variational procedure, is $-0.17$ ev, regardless of which approximation function is used for $V$. $A$ is again 2.346. Thus the calculated optical transition energy is on the order of 3.1 ev.

Two other conclusions of greater significance than the numerical magnitudes can be drawn from this discussion, however. First, the use of this artificial potential energy function has demonstrated that using the Thomas-Fermi potential energy function can be expected to give reasonable results for the calculated energy level values. Second, the tedium of the self-consistent method, that is the use of
p in the expression for V, can be eliminated, by introducing a simple
function for p, without appreciably affecting the magnitudes of the
calculated energy levels.
III. CALCULATIONS BASED ON THE THOMAS–FERMI MODEL OF POSITIVE IONS

Thomas–Fermi Equation (9)

The model of Thomas (32, p. 542-543) and Fermi (7, p. 73-75), used in their independent derivations of the equation bearing their names, pictures an atomic system as a continuous distribution of electronic charge about the nucleus, at the absolute zero of temperature. Only the electrostatic interaction between the electrons is taken into account; other factors, such as relativistic effects and exchange, are ignored.

The following simplified deduction of the Thomas–Fermi equation is patterned after the comments of Gombás (9, p. 3-5, 34-35). (The equations are written in normal units.) The total energy of an electron at any point in the atomic system is \( \frac{p^2}{2m} - e \phi_e \), where \( p \) is the electron's momentum, and \( \phi \) is the statistical potential of the nucleus and all the electrons at the point occupied by the electron in question. Let the highest possible potential energy of any electron in the system be represented by \( -\phi_e \). \( \phi_e \) is thus the lowest possible potential. For any electron to remain bound in the system, the inequality

\[
\frac{p^2}{2m} - \phi_e \leq -\phi_e
\]

must be satisfied; thus, electrons can occupy all states for which

\[
p \leq \sqrt{2m_e (\phi - \phi_e)}
\]
If all these states are assumed filled, then

\[ p_{\text{max}} = \sqrt{2m_e (\phi - \phi_o)} \]

These filled states may be considered to be contained in a sphere of momentum space with radius \( p_{\text{max}} \). Since there are 2 electrons per each \( h^3 \) of phase space volume, the charge density of the electron gas is

\[ \rho = \frac{4 \pi 4 \pi p_{\text{max}}^2}{h^3/2} (-e) = -\frac{8 \pi}{3 \hbar^3} (2m)^{3/2} \frac{\hbar^3}{2} (\phi - \phi_o)^{3/2} \]

The application of Poisson's equation, \( \nabla^2 \phi = -4 \pi \rho \), results in the relation

\[ \nabla^2 \phi = \nabla^2 (\phi - \phi_o) = \frac{32 \pi^2}{3 \hbar^3} (2m)^{3/2} \frac{\hbar^3}{2} (\phi - \phi_o)^{3/2} \]

The first equation obtains because \( \phi_o \) is a constant. The second is the Thomas-Fermi equation.

For purposes of this work, further discussion of this equation can be restricted to describing positive ions. At points very close to the nucleus the potential is \( Z e/r \); thus one boundary condition that the solution must satisfy is

\[ \lim_{r \to 0} \nabla \phi = Z e \]

Outside the ion the potential is \( (Z-N)e/r \); two other boundary conditions are obtained by demanding that the potential and its derivative be continuous at the transition point between these two expressions—the ion radius, \( R \).
\[ \phi(R) = \frac{(Z-N)\phi}{R} \]

and
\[ \left( \frac{d\phi}{dr} \right)_{r=R} = -\frac{(Z-N)\phi}{R^2} \]

It is also apparent that \( \phi_0 \) must be equal to \( \phi(R) \).

The equation and boundary conditions can easily be rewritten in atomic units, giving
\[ \nabla^2 (\phi - \phi_0) = \frac{8\sqrt{2}}{3\pi} (\phi - \phi_0)^{3/2} \]

\[ \lim_{r \to 0} r\phi = Z \]

\[ \phi(R) = \frac{Z-N}{R} \]

and
\[ \left( \frac{d\phi}{dr} \right)_{r=R} = -\frac{Z-N}{R^2} \]

If another change of variables is made, namely
\[ r = \frac{1}{4} \left( \frac{q\pi^2}{2Z} \right)^{1/3} = \mu_0 x \]

and
\[ \phi - \phi_0 = \frac{Z}{\mu_0 x} \phi_{TF} \]

the Thomas–Fermi equation and the boundary conditions are transformed into the very simple form
\[ \phi_{TF}'' = \frac{\phi_{TF}^{3/2}}{x^{2/2}} \]

\[ \phi_{TF}(0) = 1 \]
\[ \Phi_{TF}(x_0) = 0, \]

and
\[ x_0 \Phi'_{TF}(x_0) = -\frac{Z-N}{Z} = -q, \]

where \( x_0 = R/\mu_0 \), and \( q \), as defined above, is known as the ionization gradient. Incidentally, the above equation and boundary conditions are valid not only for positive ions but also for neutral atoms. Of course for atoms \( q \) is zero, and for positive ions it is a positive fraction.

Analytic solutions of this equation can not be obtained, but Kobayashi (16; 17, p. 1039–1043) has obtained accurate solutions by a technique of inward numerical integration. He has tabulated both the potential and its derivative over a range of values of the ionization degree sufficient to describe all positive ions of physical interest.

Analytic Approximation of Kobayashi's Numerical Solutions

Preliminary result

In general the ionization-gradient values for which Kobayashi's solutions were obtained do not coincide with those of real ions. Linear interpolation is used to obtain the potential values for the desired magnitudes of the ionization gradient. These values of the potential are designated \( \Phi_T \).

A graph of \( \Phi_T \) versus \( x \) reveals that \( \Phi_T \) has a generally
exponential behavior except that it becomes zero for a finite value of $x$, specifically the ion radius, $x_0$. A semi-logarithmic plot still exhibits a little curvature, being concave upward, over a range of $x$ values from 0 to about $x_0/2$. At or somewhat beyond this latter point there is an inflection point, $x'$, beyond which the curvature is concave downward.

It is desired to approximate $\phi_T$ inward from $x'$ by the function

$$\phi_A = \sum_j c_j x^{-y_j}.$$

On the semi-logarithmic plot of $\phi_T$ vs. $x$, consider the straight line tangent to the curve at $x'$ and running back to the ln $\phi_T$ axis. Its equation is

$$(\ln \phi'_t = \ln A_t - y_t x),$$

and its slope is

$$m = \frac{d(ln \phi'_t)}{dx} = \frac{1}{\phi'_t} \frac{d\phi'_t}{dx} = -y_t.$$

$\phi_T$ and $\phi'_t$ coincide at $x'$, however, since they are tangent there, so

$$y_t = -\frac{\phi'_t(x')}{\phi_T(x')}.$$

The slope of the tangent can also be established by the relationship

$$m = \frac{(n \phi'_t(o) - (n \phi_T(x'))}{o - x'} = \frac{\phi'_t(x')}{\phi_T(x')}.$$

But $\phi'_t(o) = c_t$,

so $$(\ln \phi'_t(o) = \ln c_t),$$
and
\[ \ln \, C_1 = \ln \, \phi_T(x') - x' \frac{\phi_T'(x')}{\phi_T(x')} , \]
or
\[ C_1 = \phi_T(x') \exp - x' \frac{\phi_T'(x')}{\phi_T(x')} . \]

Both \( \gamma_1 \) and \( C_1 \) could now be calculated directly from

Kobayashi's tables without recourse to any graphical procedure, if

\( \phi_T \) and \( \phi_T' \), both of which he gives, were tabulated for the desired

q values. Since this is usually not the case, it is most convenient
to replace \( \phi_T' \) by \( \overline{\phi_T'} \), the average derivative over the interval 2 \( \delta \)
of which the point in question is the midpoint. Thus

\[ \overline{\phi_T'(x)} = \frac{\phi_T(x+\delta) - \phi_T(x-\delta)}{2 \delta} . \]

Then the slope of the \( \ln \phi_T \) versus \( x \) curve at any point is

approximated by

\[ m(x) = \frac{\phi_T(x+\delta) - \phi_T(x-\delta)}{2 \delta \phi_T(x)} . \]

The inflection point \( x' \) is now easily found as that \( x \) which minimizes

\( m(x) \). The slope of the desired tangent line is, therefore,

\[ m(x') = \frac{\phi_T(x'+\delta) - \phi_T(x'-\delta)}{2 \delta \phi_T(x')} . \]

The two desired constants can now be evaluated from this slope by the

relations

\[ \gamma_1 = - m(x') \]

and

\[ C_1 = \phi_T(x') \exp - x' \, m(x') . \]
Thus the two constants are obtained directly from the potential values interpolated from Kobayashi's tables.

With $\gamma_1$ and $C_1$ known, $\phi_1$ can be evaluated over the entire range of $x$, from the expression

$$\phi_1 = C_1 e^{\gamma_1 x},$$

and can then be subtracted from $\phi_T$, leaving $\phi_{R_1}$. $\gamma_2$ and $C_2$ are now obtained from $\phi_{R_1}$ in exactly the same manner, and the process is repeated until no substantial remainder is left. The last pair of constants, $\gamma_n$ and $C_n$, are estimated in a simpler fashion, however. Since $\phi_T(0) = 1$, $C_n = 1 - C_1 - C_2 - \ldots - C_{n-1}$. $\gamma_n$ is evaluated from a plot of $\log \phi_{R_{n-1}}$ versus $x$.

$$\log \phi_{R_{n-1}} = \log C_n - \frac{\gamma_n}{2.303} x.$$  

Therefore $\gamma_n = -2.303$ times the slope.

Each succeeding $\gamma_j$ value is larger than the preceding ones. Nevertheless each exponential term makes some contribution to $\phi_A$ in the region outside the range of $x$ values it was adjusted to fit. Consequently, this means of replacing $\phi_T$ by an analytic function is somewhat approximate in nature. This arbitrariness can be reduced by using the principle of least squares, in a form discussed by Margenau and Murphy (19, p. 517-518).

Least squares refinement

In the preceding section an essentially graphical method of evaluating the $\gamma_j$'s and $C_j$'s was presented. In this section a least squares procedure is used to adjust these constants to their best
values. Denote the adjusted constants by $\gamma_j^0$ and $C_j^0$, and define the following functions:

$$\phi_A (Y_j^0, C_j^0) = \phi_F,$$

and

$$\phi_A (Y_j, C_j) = \phi_G.$$

The deviation of the potential calculated with the adjusted constants, from the potential interpolated from Kobayashi's tables is

$$d_i = \phi_T(x_i) - \phi_F(x_i).$$

(The subscript $i$ refers to the various values considered by Kobayashi for the independent variable $x_i$.) The least squares principle demands the minimization of

$$\sum_i d_i^2.$$

Now

$$\phi_F(x_i) = \phi_G(x_i) + \sum_j \left[ \frac{\partial \phi_G(x_i)}{\partial Y_j} dY_j + \frac{\partial \phi_G(x_i)}{\partial C_j} dC_j \right]$$

if derivatives of second and higher orders are neglected. $dY_j$ and $dC_j$ may be replaced, respectively, by $\gamma_j^i$ and $C_j^i$, where these latter are the desired small correction terms defined by the relations

$$\gamma_j^0 = \gamma_j + \gamma_j^i, \quad C_j^0 = C_j + C_j^i.$$ 

If the partial differential coefficients are indicated by $u_{ji}$ and $v_{ji}$, respectively, the deviation can finally be written as

$$d_i = \phi_T(x_i) - \phi_G(x_i) - \sum_j (u_{ji} \gamma_j^i + v_{ji} C_j^i).$$
Then
\[ \sum_{i} \delta_{i}^{2} = \sum_{i} \left( \sum_{j} (u_{ji} Y_{ji} + v_{ji} c_{ji}) + \Phi_{G}(x_{i}) - \Phi_{T}(x_{i}) \right)^{2}. \]

Differentiation, equation to zero, and division by two result in
\[ \sum_{i} \left\{ \sum_{j} (u_{ji} Y_{ji} + v_{ji} c_{ji}) + \Phi_{G}(x_{i}) - \Phi_{T}(x_{i}) \right\} \omega_{ki} = 0, \]
where \( w_{ki} \) is one of the \( u_{ji} \) or \( v_{ji} \). There is one equation for each \( u_{ji} \) and one for each \( v_{ji} \), \( 2j \) equations in all.

From their definitions it is apparent that
\[ \mu_{ji} = -c_{j} x_{i} e^{-y_{j} x_{i}}, \]
and
\[ \nu_{ji} = a^{-y_{j} x_{i}}. \]

These 2j simultaneous equations are equivalent to the matrix equation
\[ (\gamma_{1}', \gamma_{2}', \ldots, \gamma_{j}', c_{1}', c_{2}', \ldots, c_{j}') \mathbf{a} = (h_{1}, h_{2}, \ldots, h_{2j}), \]
where \( \mathbf{a} \) is a 2j x 2j matrix. The typical element of \( \mathbf{a} \), \( a_{jk} \), is readily computed from the relation
\[ a_{jk} = \sum_{l} \omega_{jl} \omega_{kl} ; \]
the typical element, \( h_{k} \), of the row matrix \( \mathbf{h} \) is determined from the relation
\[ h_{k} = \sum_{i} \left\{ \Phi_{T}(x_{i}) - \Phi_{G}(x_{i}) \right\} \omega_{ki}. \]

Evidently \( a_{jk} = a_{kj} \); that is to say, \( \mathbf{a} \) is symmetric.

The matrix \( \mathbf{a} \) can be reduced to a triangular matrix, or one with its rows interchanged, through postmultiplication by \( 2j - 1 \).
carefully selected matrices. The procedure has been discussed thoroughly by Frazer, Duncan, and Collar (8, p. 126-127), and it will be illustrated here for a $3 \times 3$ matrix; extension to higher orders is not difficult.

\[
\begin{pmatrix}
  c_1 & c_2 & c_3 \\
  a_{11} & a_{12} & a_{13} \\
  a_{21} & a_{22} & a_{23} \\
  a_{31} & a_{32} & a_{33}
\end{pmatrix}
\begin{pmatrix}
  h_1 \\
  h_2 \\
  h_3
\end{pmatrix}
\]

Postmultiply both sides by \[
\begin{pmatrix}
  1 & -a_{22}/a_{21} & -a_{23}/a_{21} \\
  0 & 1 & 0 \\
  0 & 0 & 1
\end{pmatrix};
\]

then

\[
\begin{pmatrix}
  c_1 & c_2 & c_3 \\
  a_{11} & b_{11} & b_{12} \\
  a_{21} & 0 & 0 \\
  a_{31} & b_{21} & b_{22}
\end{pmatrix}
\begin{pmatrix}
  h_1 \\
  h_2 \\
  h_3
\end{pmatrix}
\]

Now postmultiply both sides of this last equation by

\[
\begin{pmatrix}
  1 & 0 & 0 \\
  0 & 1 & -b_{22}/b_{21} \\
  0 & 0 & 1
\end{pmatrix};
\]

then

\[
\begin{pmatrix}
  c_1 & c_2 & c_3 \\
  a_{11} & b_{11} & c_{11} \\
  a_{21} & 0 & 0 \\
  a_{31} & b_{21} & 0
\end{pmatrix}
\begin{pmatrix}
  h_1 \\
  h_2 \\
  h_3
\end{pmatrix}
\]

The square matrix is now in triangular form with the rows
interchanged (placing the top row on the bottom will produce a
triangular matrix), and the solutions for \( C_j \) are easily obtained.

\[
C_1c_{11} = h_3'', c_1 = h_3''c_{11},
\]

\[
C_1b_{11} + C_3b_{21} = h_2', C_3b_{21} = h_2' - b_{11}h_3''c_{11},
\]

\[
C_3 = h_2'/b_{21} - b_{11}h_3''/b_{21}c_{11}.
\]

\[
C_1a_{11} + C_2a_{21} + C_3a_{31} = h_1, C_2a_{21} = h_1 - a_{11}h_3''/c_{11} - a_{31}h_2'/b_{21}
\]

\[
+ a_{31}b_{11}h_3''/b_{21}c_{11}, C_2 = h_1/a_{21} - a_{11}h_3''/a_{21}c_{11} - a_{31}h_2'/a_{21}b_{21}
\]

\[
+ a_{31}b_{11}h_3''/a_{21}b_{21}c_{11}.
\]

The beauty of this procedure is the ease with which it can
be carried out on a desk calculator. The operations described above
for triangularizing a matrix are contained in the array below.

\[
\begin{array}{ccc|ccc}
  h_1 & h_2 & h_3 \\
  a_{11} & a_{12} & a_{13} & -a_{22}/a_{21} & -a_{23}/a_{21} \\
  *a_{21} & a_{22} & a_{23} & & & 1 & 0 \\
  a_{31} & a_{32} & a_{33} & 0 & 1 & \hline
  h_2' & h_3' \\
  b_{11} & b_{12} & -b_{22}/b_{21} & \hline
  *b_{21} & b_{22} & & & & 1 \\
  h_3'' & c_{11} & & & \end{array}
\]

The arrays to the left of the vertical line, exclusive of the
asterisked rows, are postmultiplied by the arrays to the right of
the vertical line and on the same level, to obtain the arrays directly
below. The rules of matrix multiplication apply, of course. The
elements of the row matrix \( \mathbf{f} \) are obtained similarly.
Once the entire arrangement has been enumerated, the triangular matrix can be written down directly; the solutions are then obtained as above.

This method has been used to evaluate the empirical constants in the analytic approximation of the potential for Ca$^{+2}$ and Sr$^{+2}$; in both instances $j$ is taken equal to 4. The magnitude of the maximum percentage deviation of $\phi_F$ from $\phi_T$ is about 0.2% over the range of $x$ values from the nucleus to half the crystallographic ionic radius. Over the rest of the range, it is on the order of 1%, because the potential itself becomes quite small. The values of these constants are given in Table 6.

**Table 6**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Ca$^{+2}$</th>
<th>Sr$^{+2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>0.31378</td>
<td>0.24504</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>1.15604</td>
<td>0.87708</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>3.9461</td>
<td>2.9401</td>
</tr>
<tr>
<td>$\gamma_4$</td>
<td>12.204</td>
<td>19.639</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.36007</td>
<td>0.24608</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.50674</td>
<td>0.52997</td>
</tr>
<tr>
<td>$C_3$</td>
<td>0.11366</td>
<td>0.20565</td>
</tr>
<tr>
<td>$C_4$</td>
<td>0.01888</td>
<td>0.01848</td>
</tr>
</tbody>
</table>

Modification of the Thomas-Fermi Radius

The total potential for $r \leq R$ can now be written

$$\phi = \frac{Z}{Y} \phi_F + \frac{Q}{R},$$
in atomic units, where \( \phi_F' \) of course, is the analytic expression for the potential as derived above. Application of Poisson's equation to the part of this total potential that arises from the electrons gives for the electronic charge density

\[
\rho_e = -\frac{Z}{4\pi Y} \phi_F''.
\]

If \( \phi_F \) is the exact solution of the Thomas-Fermi equation, and if the ionic radius is that predicted by the theory, \( R_{TF} \), then

\[
\int_0^{R_{TF}} \rho_e \, d\tau = -Z \int_0^{R_{TF}} \nu \phi_F'' \, dY = -(Z - q).
\]

This can also be written

\[
\int_0^{R_{TF}} \nu \phi_F'' \, dY = 1 - q.
\]

It turns out that \( R_{TF} \) is roughly twice as large as the crystallographic ionic radius, \( R \), however. Since it is certain that the actual ionic radius will not be \( R_{TF} \), but something reasonably close to \( R \), \( R \) will be accepted, without change, as the actual ionic radius. In effect, this change in the ionic radius compresses the charge distribution; none of the charge predicted by the Thomas-Fermi theory to lie between \( R \) and \( R_{TF} \) will be there. The problem at hand, then, is to modify the potential, \( \phi_F \), to reflect this change in the charge distribution.

The simplest approach to try is that of leaving the potential unchanged but cutting it off at \( R \). This is satisfactory only if the magnitude of the charge lying between \( R \) and \( R_{TF} \) is quite small. This magnitude is
\[-(z - q) - \int_0^R p_\alpha \, dr\]

\[= -(z - q) + \int_0^R z \gamma \phi_F'' \, dr\]

\[= Q + Z \left\{ R \phi_F' (R) - \phi_F (R) \right\}.\]

The validity of this expression can be checked by replacing \(R\) with \(R_{TF}\), in which case it should reduce to zero, since there can be nothing between \(R_{TF}\) and \(R_{TF}\). Using the boundary conditions,

\[\phi_F (0) = 1, \quad \phi_F (R_{TF}) = 0, \quad \text{and} \quad R_{TF} \phi_F' (R_{TF}) = -q,\]

gives

\[Q + Z (-q - a) = Q + Z \left( -\frac{q}{Z} \right) = Q - q = 0\]

as required.

In general, for the crystallographic ionic radius, \(R\),

\[\phi_F (R) > 0,\]

\(R\) is on the order of \(1/2 R_{TF}\), and

\[\left| \phi_F' (R) \right| > 2 \left| \phi_F' (R_{TF}) \right|\]

This means that the bracketed term is more negative than \(-q\), and hence some negative charge exists between \(R\) and \(R_{TF}\). The magnitude of this charge can be determined roughly by using values estimated directly from Kobayashi's tables. For \(Ca^+2\) and \(Sr^+2\) the result is about \(-2\), that is, the charge of two electrons. This seems too large to ignore.
Another simple possibility, however, is that of changing the potential somewhat to be consistent with the increased charge density within the sphere of radius $R$. One way to do this is to modify the potential function to read

$$\phi_M = \left\{ 1 - B\left(\frac{R}{r}\right)^n \right\} \phi_F \frac{Z}{r} + \frac{Q}{R},$$

where $n$ is an arbitrary integer, and $B$ is a constant which will be evaluated from Poisson's equation by demanding that electronic charge be conserved.

$$\rho_{M,l} = -\frac{1}{4\pi} \nabla^2 \phi_M,\quad l$$

$$\int_0^R \rho_{M,l} dr = -(Z - Q),$$

$$\int_0^R (\nabla^2 \phi_M) r^2 dr = -(Z - Q),$$

$$\int_0^R \frac{d}{dr} (r^2 \phi_M') dr = Z - Q,$$

and finally

$$r^2 \frac{d \phi_M}{dr} \Big|_0^R = Z - Q.$$

$B$ can be evaluated from this last equation.

$$\phi_{M,2} = \phi_M - \frac{Z}{r}$$

$$= \frac{Z}{r} \phi_F - \frac{ZB}{R^n} r^{n-1} \phi_F' + \frac{Q}{R} - \frac{Z}{r},$$

$$\frac{d \phi_{M,2}}{dr} = -\frac{Z}{r^2} \phi_F + \frac{Z}{r} \phi_F' - (n-1) \frac{ZB}{R^n} r^{n-2} \phi_F' - \frac{ZB}{R^n} r^{n-1} \phi_F' + \frac{Z}{r^2},$$
\[ y^2 \frac{d^2 \Phi_{M,0}}{dy^2} = -Z \Phi_F + Z y \Phi_F' - (n-1) \frac{Z B}{R^n} r^n \Phi_F - \frac{Z B}{R^n} r^{n+1} \Phi_F' + Z, \]

\[ y^2 \frac{d^2 \Phi_{M,k}}{dy^2} \bigg|_o = -Z \Phi_F(R) + Z + Z R \Phi_F'(R) - (n-1) Z B \Phi_F(R) - Z B R \Phi_F'(R), \]

\[ \frac{Z - \Phi}{Z} = 1 - \Phi = -\Phi_F(R) + 1 + R \Phi_F'(R) - (n-1) B \Phi_F(R) - B R \Phi_F'(R), \]

and

\[ B = \frac{\Phi + R \Phi_F'(R) - \Phi_F(R)}{(n-1) \Phi_F(R) + R \Phi_F'(R)}. \]

In this evaluation of B it has been assumed that \( \Phi_F \) satisfies the Thomas-Fermi equation exactly. In actuality this is not quite the case; of importance here is the fact that \( \Phi_F \) satisfies the boundary condition \( \Phi_{TF}(\sigma) = 1 \) only approximately. Thus a better enumeration of B can be obtained from the relationship

\[ B = \frac{\Phi - 1 + \Phi_F(\sigma) + R \Phi_F'(R) - \Phi_F(R)}{(n-1) \Phi_F(R) + R \Phi_F'(R)}. \]

It still remains to choose the value of n. This compression of electronic charge into a smaller volume means that \( \rho_{M,2} \) is more negative than \( \rho_2 \), and as a result, \( \Phi''_M \leq \Phi''_F \). \( \Phi''_F \) is of course the derivative of the slope of the \( \Phi_F \) versus r curve. \( \Phi'_F \) is everywhere negative, but increasing, so \( \Phi''_F \) is everywhere positive. For \( \Phi''_M \) to be everywhere more positive than \( \Phi''_F \) requires that \( \Phi'_M \) be everywhere more negative than \( \Phi'_F \). Thus \( \Phi'_M \) falls off
more rapidly than $\phi_F$ and lies below it for all $r$ except $r=0$. This can be the case only if $B$ is positive.

As is evident from earlier arguments the numerator of the expression for $B$ is negative, as is the second term in the denominator. The first term of the denominator is positive, however, and for sufficiently large $n$ the denominator passes from negative to positive. This change from positive $B$ to negative $B$ occurs at about $n=3$, so $n$ is restricted in value to either 1 or 2.

With $n=1$, $B$ for $Ca^{+2}$ is 0.71676 and for $Sr^{+2}$, 0.77126, while with $n=2$, the values are 1.64313 for $Ca^{+2}$ and 1.53764 for $Sr^{+2}$. Satisfaction of the boundary condition, $\phi_M(R) = \Phi/R$, demands that $B=1$, of course. Thus, using $n=2$ introduces 2 to 3 times the error at $r=R$ that using $n=1$ does. On the other hand, $n=2$ has the advantage of disturbing the potential less in the inner part and more in the outer part of the electron cloud. $n=2$ also has the advantage of giving rise to a much smaller discontinuity in the potential at $R$. As a result of these considerations, $n$ is taken to be 2, and the corresponding $B$ values are used.

In Figures 3 and 4 are plotted $\phi_T$, $\phi_F$, and $\phi_M$ for $Ca^{+2}$ and $Sr^{+2}$. Two aspects of the preceding discussions are illustrated by this graph: (1) the deviation of $\phi_F$ from $\phi_T$, and (2) the effect of the compression of charge within the crystallographic radius.

Polarization

In addition to the field of the impurity cation, the trapped
Fig. 3.—Potential functions for Ca$^{+2}$
Fig. 4.--Potential functions for Sr$^{+2}$
electron, while in the cavity, also experiences the field of the other (unpolarized) ions plus the field of the polarization. The potential from the former source is simply the Madelung potential and contributes the amount $a/a_0$ to the electron's potential energy. The potential from the latter source is sometimes called the Jost potential and will now be evaluated.

The Jost potential is the potential at the impurity cation site arising from the polarization of the lattice about this defect. It is applicable only when the electron is within the cavity. On the other hand, the field in which the electron moves when outside the cavity, is, at a given point, the field existing when the electron is at that point. The field formula already used in describing the electron's motion outside the cavity must be modified to reflect any relaxation of the lattice before it can be applied to estimate the Jost potential. As before, it is assumed that ions move too slowly to follow the electronic motion; on the other hand, the polarization of the electron clouds can certainly follow it. Consequently, when the electron is at or near the center of the impurity cation site, the electron cloud distortion produced by the charge it "neutralizes" will relax.

Thus, the polarization of the lattice is of two types:

1. Polarization due to displacement of ions; this remains constant as the electron moves.

2. Polarization due to distortion of electron clouds; this follows the motion of the electron.
The effective dielectric constant for the former is $-1/c$, and for the latter it is $k_0$.

Any charge the impurity cation has in excess of two units will permanently polarize the medium, regardless of the electron's position. Both types of polarization occur, so the field is $(Q-2)/r^2k$. Of the remaining units of charge, one simply replaces that of the missing host cation and exerts no polarizing influence, in first approximation. The other is considered as being partially neutralized by the electron's charge, as a function of the latter's probability distribution. The fraction of time that a given point is at a greater distance from the impurity than is the electron is $p$, while the fraction of time that it is nearer the impurity than is the electron is $1-p$. Thus, the field outside the cavity at the point occupied by the electron is

$$E = \frac{Q-2}{r^2 K} + \frac{1-p}{r^2 K} + \frac{p}{r^2 k_0} = \frac{Q-1}{r^2 K} + \frac{cp}{r^2}.$$  

When the electron returns to the cavity center, the optical polarization relaxes, so the field outside the cavity when the electron is at the cavity center is

$$E = \frac{Q-2}{r^2 K} + \frac{1-p}{r^2 K} (-c) = \frac{Q-1}{r^2 K} + \frac{cp}{r^2} - \frac{1}{r^2 k_0}.$$  

It is this latter field which gives rise to the Jost potential. Rewriting these fields in the slightly different form,

$$E = -c \frac{Q-1}{r^2} + \frac{Q-1}{r^2 K_0}$$

for the electron at $r$, and
\[
E = -e \frac{Q-1}{r^2} + \frac{Q-2}{r^2 \kappa_0}
\]

for the electron at the cavity center, delineates the contribution of each type of polarization to the fields. In each of the above equations the first term arises from the low-frequency polarization and the second from the optical polarization. It is convenient to consider these two types of polarization separately. The optical polarization will be treated first.

Consider an effective unit positive charge in the cavity, with a spherically symmetric distribution about the cavity center. Outside the cavity the electric displacement is \( D = 1/r^2 \) and the electric field is \( E = 1/r^2 \kappa_0 \). The polarization is, therefore,

\[
P = \frac{1}{4\pi} \left(1 - \frac{1}{\kappa_0}\right) \frac{1}{r^2},
\]

and the potential inside the cavity arising from this polarization,

\[
\phi = -\int_R^\infty \frac{P}{r^2} 4\pi r^2 dr = \left(1 - \frac{1}{\kappa_0}\right) \int_R^\infty \frac{dr}{r^2} = -\frac{1}{R} \left(1 - \frac{1}{\kappa_0}\right).
\]

For the electron at infinity, the charge in the cavity is \( Q - 1 \), and the potential is

\[
(Q-1) \phi = -\frac{Q-1}{R} \left(1 - \frac{1}{\kappa_0}\right),
\]

but with the electron in the cavity, the charge in the cavity is \( Q-2 \), and the potential is

\[
(Q-2) \phi = -\frac{Q-2}{R} \left(1 - \frac{1}{\kappa_0}\right).
\]

Thus the potential depends upon the amount of charge in the cavity,
and the contribution to the electron's potential energy from this optical polarization is

\[ V_{\text{OPT}} = -\frac{1}{R} (1 - \frac{1}{K_0}) \int_{Q-1}^{Q-2} q dq = \frac{Q - \frac{3}{2}}{R} (1 - \frac{1}{K_0}). \]

This is essentially the electrostatic energy of adding a charge to the cavity.

The contribution to the electron's potential energy from the low frequency polarization is

\[ V_{\text{Low}} = \int_{-\infty}^{R} c \frac{Q - \frac{1}{2} - p}{r^2} dr = \frac{Q - \frac{3}{2}}{R} c + c \int_{R}^{\infty} \frac{1 - p}{r^2} dr. \]

The total polarization energy, then, is

\[ V_{\text{POL}} = \frac{1}{R} (Q - \frac{3}{2} - \frac{Q - \frac{2}{2}}{K} - \frac{1}{2K_0}) + c \int_{R}^{\infty} \frac{1 - p}{r^2} dr. \]

If the electron is always in the cavity, \( p = 1 \) for all \( r>R \); thus the integral is zero, and the polarization energy is equal to the first term. This assumption is usually made in F-center calculations.

If \( Q \) is set equal to 2 in the above expression, which makes it valid for both an anion vacancy and a substitutional divalent cationic impurity since both have an effective polarizing charge of 1,

\[ V_{\text{POL}} = \frac{1}{2R} (1 - \frac{1}{K_0}), \]

the customary form of the Jost potential energy.

In the present problem, however, \( p \) is quite small in the
cavity, and the above assumption is certainly not valid. In the next section arguments are presented for approximating $1 - p$ by $R/r$. When this substitution is made, evaluation of the integral gives $1/2R$, and the polarization energy becomes

$$V_{pol} = \frac{1}{R} \left( \Phi - \frac{3}{2} - \frac{\Phi}{K} \right).$$

It is rather interesting to observe that, since the integral has a minimum value of zero and a maximum value of $1/R$, this result is the average of all possible values for the polarization energy. For Sr$^{+2}$ and Ca$^{+2}$ $Q = 2$, and the polarization, or Jost, potential energy is

$$V_{pol} = \frac{1}{2R} \left( 1 - \frac{1}{K} \right).$$

Approximations for $p$ and the Field outside the Cavity

If the self-consistent approach is used, the field outside the cavity is found to be

$$F = \frac{\phi - 1}{V^2K} + \frac{c \phi}{V^2},$$

as was shown earlier. At the cavity edge $p$ is on the order of a few hundredths, and for very large values of $r$ it is essentially unity. A function having the same limiting behavior as $p$ is

$$1 - \left( \frac{R}{V} \right)^n,$$

where $n$ is restricted to integral values to facilitate later manipulations. Although $n$ is arbitrary, there seems to be no unique way of enumerating it, so it will be taken as unity for the sake of simplicity. Thus, $p = 1 - R/r$. 
Substituting this value of \( p \) into the self-consistent expression for \( E \) results in

\[
E = \frac{1}{r^2} \left( \frac{Q-2}{K} + \frac{1}{K_0} \right) - \frac{Rc}{Y^3}.
\]

With this approximate expression, the field becomes \((Q-1)/r^2k\) for values of \( r \) near \( R \), while for large values of \( r \) it approaches

\[
\frac{1}{r^2} \left( \frac{Q-2}{K} + \frac{1}{K_0} \right).
\]

A potential function which exhibits a corresponding limiting behavior is

\[
\phi = \frac{1}{r} \left( \frac{Q-2}{K} + \frac{1}{K_0} \right) - \frac{Rc}{Y^2}.
\]

These two functions are inconsistent with one another, however. The functions are related as follows:

If

\[
E = \frac{1}{r^2} \left( \frac{Q-2}{K} + \frac{1}{K_0} \right) - \frac{Rc}{Y^3}, \tag{1}
\]

then

\[
\phi = \frac{1}{r} \left( \frac{Q-2}{K} + \frac{1}{K_0} \right) - \frac{Rc}{2r^2}.
\]

But

\[
E = \frac{1}{r^2} \left( \frac{Q-2}{K} + \frac{1}{K_0} \right) - \frac{2Rc}{Y^3}, \tag{2}
\]

if

\[
\phi = \frac{1}{Y} \left( \frac{Q-2}{K} + \frac{1}{K_0} \right) - \frac{Rc}{Y^2}.
\]

These two \( E, \phi \) pairs will be recognized as those used previously with the artificial potential function in an effort to eliminate the labor of the self-consistent procedure. The energies calculated with these approximations were very close to that calculated by the self-consistent method, the energy from \((1)\) being a little low, and that from \((2)\), a little high.

In addition to these pairs for \( E \) and \( \phi \), there are three others worth considering:
These three pairs have been selected because they lie somewhat close in value to (1) and (2); (3) lies between them, while (4) lies below (2), and (5) lies above (1). Were the only aim the selection of that pair which best reproduces the results of the self-consistent method, then (3) would be the logical choice. There is one other factor to be considered, however—essentially a criticism of the original derivation of the field expression.

Inside the cavity the effective charge of the impurity cation has been taken as the actual charge, a procedure which is certainly reasonable. Outside the cavity the effective charge has been taken as one less than the actual charge, since the charge effective in polarizing the medium is that charge in excess of the normal charge. This procedure is unquestionably valid at great distances from the
site of the defect, but it seems rather crude in the vicinity of the defect. To say that the effective charge is $Q$ for $r$ slightly less than $R$, but only $Q - 1$ for $r$ slightly greater than $R$, seems ludicrous. Rather, it seems that a reasonable field expression should contain $Q$ as the effective charge for $r$ near $R$ and $Q - 1$ for very large $r$.

It will be noticed, that for $r$ very much greater than $R$, all five of the above $E$, $\phi$ pairs display the same limiting behavior, namely

$$E = \frac{1}{Y^2} \left( \frac{Q - 2}{K} + \frac{1}{K_0} \right), \quad \phi = \frac{1}{Y} \left( \frac{Q - 2}{K} + \frac{1}{K_0} \right).$$

This is precisely the form expected for an effective charge of $Q - 1$; thus, all five pairs are equally valid in describing the field at large values of $r$. The limiting behavior at the cavity edge, that is for $r = R$, differs markedly from one to the other, however, as is indicated below. The relationships on the right hand side are obtained by using the approximation $k = 2k_0$.

$$\phi = \frac{Q - 3/2}{rK} + \frac{1}{2YK_0}, \quad E = \frac{Q - 1}{Y^2K}, \quad \phi \sim \frac{Q - \sqrt{2}}{YK}, \quad E \sim \frac{Q - 1}{Y^2K}. \quad (1')$$

$$\phi = \frac{Q - 1}{rK}, \quad E = \frac{Q}{Y^2K} - \frac{1}{Y^2K_0}; \quad \phi = \frac{Q - 1}{rK}, \quad E \sim \frac{Q - 2}{Y^2K}. \quad (2')$$

$$\phi = \frac{Q - 1/2}{rK}, \quad E = \frac{Q + 1}{Y^2K} - \frac{1}{Y^2K_0}; \quad \phi = \frac{Q - 1/2}{rK}, \quad E \sim \frac{Q - 1}{Y^2K}. \quad (3')$$

$$\phi = \frac{Q - 3/2}{rK}, \quad E = \frac{Q - 1}{Y^2K} - \frac{1}{Y^2K_0}; \quad \phi = \frac{Q - 3/2}{rK}, \quad E \sim \frac{Q - 3}{Y^2K}. \quad (4')$$

$$\phi = \frac{Q}{rK}, \quad E = \frac{Q + 2}{Y^2K} - \frac{1}{Y^2K_0}; \quad \phi = \frac{Q}{rK}, \quad E \sim \frac{Q}{Y^2K}. \quad (5')$$
It seems that \( (5') \) is the most reasonable choice for the following two reasons: it is the only pair in which the expressions for field and potential involve the same charge, and it is the only pair in which the charge involved is the actual charge of the impurity cation. Thus, the electron's potential energy when outside the cavity is given by

\[
V = -\frac{1}{Y} \left( \frac{Q - Z}{K} + \frac{1}{K_0} \right) + \frac{R}{r^2} \left( \frac{1}{K_0} - \frac{2}{K} \right).
\]

It should be emphasized that the above arguments constitute a rederivation of \( V \), not an approximation to \( p \). \( p \) will be essentially unaffected by this change, ranging in value from a few hundredths near \( R \) to essentially unity for large \( r \). To emphasize this, \( V \) may be rewritten in the form

\[
V = -\frac{\Phi}{RK} - \frac{P}{Y} \left( \frac{1}{K_0} - \frac{2}{K} \right).
\]

For \( r \) near \( R \), \( p \) is small, and \( V \) approaches \(-\Phi/2K\), while for large \( r \), \( p \) is unity, and \( V \) becomes

\[
-\frac{1}{Y} \left( \frac{Q - 2}{K} + \frac{1}{K_0} \right).
\]

This is precisely the behavior desired of \( V \). If \( p \) is still approximated by \( 1 - R/r \) in the latter equation for \( V \), the former equation is obtained.

**Derivations and Results**

The potential energy functions, as determined by the preceding arguments, are
\[ V = (B \frac{r^2}{R^2} - 1) \frac{Z}{\gamma} \sum_{i=1}^{4} (c_i e^{-\gamma_i r}) - V_o, \quad 0 \leq r \leq R, \]

\[ V = -\frac{1}{\gamma} \left( \frac{Q-2}{K} + \frac{1}{K_o} \right) + \frac{R}{\gamma^2} \left( \frac{1}{K_o} - \frac{2}{K} \right), \quad R \leq r \leq \infty, \]

where \[ V_o = \frac{\Phi}{R} - \frac{\alpha}{a_o} - \frac{1}{2R} \left( 1 - \frac{1}{K} \right). \]

The computations are carried out for Ca\(^{+2}\) and Sr\(^{2+}\), both in sodium chloride and potassium chloride. The values of \( C_j \) are still the same as given in Table 6, but the transformation of the potential energy function back to atomic units gives rise to the new values of \( \gamma_j \) given in Table 7.

### Table 7

<table>
<thead>
<tr>
<th>Constant</th>
<th>( \text{Ca}^{+2} )</th>
<th>( \text{Sr}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_1 )</td>
<td>0.96204</td>
<td>0.93051</td>
</tr>
<tr>
<td>( \gamma_2 )</td>
<td>3.54437</td>
<td>3.33060</td>
</tr>
<tr>
<td>( \gamma_3 )</td>
<td>12.0986</td>
<td>11.1647</td>
</tr>
<tr>
<td>( \gamma_4 )</td>
<td>37.417</td>
<td>74.577</td>
</tr>
</tbody>
</table>

Some idea of the degree of consistency of the potential energy representation of the impurity cation core can be obtained by the following procedure. From the function as given determine the electronic density by application of Poisson's equation, and
integrate this density from $0$ to $R$. The result is

$$
\int_0^R \rho d\tau = \sum_{i=1}^4 \left[ -Y_e R \left\{ B Z C_\lambda (1-Y_e R) + Z C_\lambda (1+Y_e R)-Z C_\lambda \right\} \right].
$$

Since all the electronic charge in the ion lies between $0$ and $R$, this integral should equal $-N$, where $N$ is the electron number; the degree to which the above summation approximates $-N$ is thus a direct measure of its consistency. For Ca$^{+2}$ the summation gives $-20.000$, and for Sr$^{+2}$, $-36.006$; the corresponding values of $N$ are 20 and 36, respectively.

The trial wave functions used for Ca$^+$ are the 4s and 4p hydrogen-like wave functions already given. The corresponding 5s and 5p functions are used for Sr$^+$.

$$
\psi_{50} = \left( \frac{\lambda_{50}}{2Z_{50}} \right)^{\frac{1}{2}} \left( 15 - 60 \lambda_{50} V + 60 \lambda_{50}^2 V^2 - 20 \lambda_{50}^3 V^3 + Z \lambda_{50}^4 V^4 \right) e^{-\lambda_{50} R},
$$

$$
\psi_{51} = \left( \frac{2 \lambda_{51}}{2Z_{51}} \right)^{\frac{1}{2}} \cos \theta V \left( 30 - 45 \lambda_{51} V + 18 \lambda_{51}^2 V^2 - 2 \lambda_{51}^3 V^3 \right) e^{-\lambda_{51} V}.
$$

Substitution of $V$ and one of the wave functions, $\psi_{nl}$, into the variation integral and minimization of $W$ with respect to the variation parameter, $\lambda_{nl}$, lead to the following expressions for $W_{nl}$ and its derivative:
\[ \lambda_{nl} + \sum_{i=1}^{4} \left[ \sum_{k=1}^{2n+3} \left\{ \left( \frac{\lambda_{nl}}{k} \right)^{2n+3-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \right] \]

\[ + N Z C \sum_{k=1}^{2n+1} \left\{ \left( \frac{\lambda_{nl}}{2n+1} \right)^{2n+1-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \]

\[ + \frac{N B Z C}{\lambda_{nl} R^2} P_{_3} \left( \frac{\lambda_{nl}}{2n+1} \right) - N Z C \sum_{k=1}^{2n+3} \left\{ \left( \frac{\lambda_{nl}}{2n+3} \right)^{2n+3-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \]

\[ + \frac{-k V}{S} \sum_{k=1}^{2n} \left\{ \left( \frac{\lambda_{nl}}{2n} \right)^{2n-k} \right\} P_{_k} \left( \lambda_{nl} R \right) - \frac{1}{T K_0} \sum_{k=1}^{2n} \left\{ \left( \frac{\lambda_{nl}}{2n} \right)^{2n-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \]

\[ = 0, \]

\[ W_{nl} = \frac{\lambda_{nl}^2}{2} + \sum_{i=1}^{4} \left[ \sum_{k=1}^{2n+2} \left\{ \left( \frac{\lambda_{nl}}{k} \right)^{2n+2-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \right] \]

\[ + N Z C \sum_{k=1}^{2n+1} \left\{ \left( \frac{\lambda_{nl}}{2n+1} \right)^{2n+1-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \]

\[ + \frac{N B Z C}{\lambda_{nl} R^2} P_{_3} \left( \frac{\lambda_{nl}}{2n+1} \right) - N Z C \sum_{k=1}^{2n+2} \left\{ \left( \frac{\lambda_{nl}}{2n+2} \right)^{2n+2-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \]

\[ + \frac{V_0}{S} \sum_{k=1}^{2n+1} \left\{ \left( \frac{\lambda_{nl}}{2n+1} \right)^{2n+1-k} \right\} P_{_k} \left( \lambda_{nl} R \right) \]

\[ = 0, \]

\[ q - 2\lambda_{nl} R - V_0. \]
n and l are the principal and azimuthal quantum numbers, respectively. N, S, T, U and Y are constants determined by the quantum state, that is by n and l; their values are given in Table 8.

**TABLE 8**

<table>
<thead>
<tr>
<th>nl</th>
<th>N</th>
<th>S</th>
<th>T</th>
<th>U</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>4/9</td>
<td>9</td>
<td>36</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>41</td>
<td>4/15</td>
<td>15</td>
<td>60</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>50</td>
<td>4/225</td>
<td>225</td>
<td>225</td>
<td>225</td>
<td>225</td>
</tr>
<tr>
<td>51</td>
<td>8/675</td>
<td>675</td>
<td>675</td>
<td>675</td>
<td>675</td>
</tr>
</tbody>
</table>

E, Z, C₁, and R are constants that depend on the particular impurity cation. k and k₀ depend only on the host lattice involved, and V₀ depends on both the impurity and the host lattice. \( P_a^b(c) \) symbolizes a polynomial in c of degree b; a is simply an index. The polynomial coefficients (all divided by 100) are listed in Appendix II.

The actual computations of this section were carried out almost exclusively on the ALWAC Model III-E computer. The solution of the derivative equation was obtained by essentially a graphical method. The entire expression was evaluated at increments of 0.1 over a range of 0 - 3.5 in the variation parameter; from these results the approximate solution was found. The expression was again evaluated, this time in increments of 0.0025 in the variation parameter, over a narrow range which included the approximate solution.
as its midpoint. From these results the solution could readily be
interpolated to the nearest 0.00001. The minimizing variation
parameter thus obtained was then used in the second equation to
determine the energy. The results are summarized in Table 9.

### TABLE 9

**VARIATION PARAMETERS AND ENERGIES**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>n_l</th>
<th>λ_{n_l}</th>
<th>W_{n_l}(ev)</th>
<th>n_l</th>
<th>λ_{n_l}</th>
<th>W_{n_l}(ev)</th>
<th>ΔW(ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl:Ca</td>
<td>40</td>
<td>0.96438</td>
<td>-4.106</td>
<td>41</td>
<td>0.11889</td>
<td>-0.185</td>
<td>3.921</td>
</tr>
<tr>
<td>KCl:Sr</td>
<td>50</td>
<td>1.45949</td>
<td>-9.121</td>
<td>51</td>
<td>0.09982</td>
<td>-0.121</td>
<td>9.000</td>
</tr>
<tr>
<td>NaCl:Ca</td>
<td>40</td>
<td>0.94719</td>
<td>-3.862</td>
<td>41</td>
<td>0.10866</td>
<td>-0.161</td>
<td>3.701</td>
</tr>
<tr>
<td>NaCl:Sr</td>
<td>50</td>
<td>1.44383</td>
<td>-8.801</td>
<td>51</td>
<td>0.09036</td>
<td>-0.105</td>
<td>8.696</td>
</tr>
</tbody>
</table>

Similar calculations were also carried out with the 3d and
4d hydrogen-like wave functions.

\[
\psi_{32} = \left( \frac{\lambda_{32}}{18\pi} \right)^{1/2} (3 \cos^2 \theta - 1) r^2 e^{-\lambda_{32} r},
\]

\[
\psi_{42} = \left( \frac{\lambda_{42}}{36\pi} \right)^{1/2} (3 \cos^2 \theta - 1) r^2 (3 - \lambda_{42} r) e^{-\lambda_{42} r}.
\]

The necessary constants are given in Table 10, the polynomial
coefficients are included in Appendix II, and the variation
parameters and energies are summarized in Table 11. No optical
transition energies are shown in Table 11 because selection rules
do not allow transitions from an s state to a d state.
TABLE 10

CONSTANTS IN \( w_{nl} \) EXPRESSION

<table>
<thead>
<tr>
<th>nl</th>
<th>N</th>
<th>S</th>
<th>T</th>
<th>U</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>8/45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>42</td>
<td>4/45</td>
<td>45</td>
<td>180</td>
<td>45</td>
<td>90</td>
</tr>
</tbody>
</table>

TABLE 11

VARIATION PARAMETERS AND ENERGIES

<table>
<thead>
<tr>
<th>Crystal</th>
<th>nl</th>
<th>( \lambda_{nl} )</th>
<th>( w_{nl}(eV) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl:Ca</td>
<td>32</td>
<td>0.15239</td>
<td>-0.324</td>
</tr>
<tr>
<td>KCl:Sr</td>
<td>42</td>
<td>0.11468</td>
<td>-0.183</td>
</tr>
<tr>
<td>NaCl:Ca</td>
<td>32</td>
<td>0.14122</td>
<td>-0.284</td>
</tr>
<tr>
<td>NaCl:Sr</td>
<td>42</td>
<td>0.10654</td>
<td>-0.161</td>
</tr>
</tbody>
</table>

Radial distribution functions are plotted in Figures 5, 6, 7, and 8 for the various cases studied.

Alternate Derivations

The integrations and differentiations indicated in the previous section are simple enough to carry out, but they do become quite tedious because of the very large number of terms. Quite a bit of time can be saved, therefore, by using a method of evaluating the derivatives which circumvents the integrations altogether. There are only two types of integral involved, so the derivation of the necessary formulas does not demand much time.
Fig. 5.—Radial distribution functions for Ca\(^+\) in KCl
Fig. 6.—Radial distribution functions for Sr⁺ in KCl
Fig. 7.—Radial distribution functions for Ca\(^+\) in NaCl
Fig. 8: Radial distribution functions for Sr⁺ in NaCl
The more tedious of the two integral types is

\[ W_{ij} = c \lambda^a \int_0^R \lambda^m y^n e^{-(z \lambda + y_i) R} \, dr, \]

where \( W_{ij} \) is the \( j \)-th term of a series of terms, \( C \) is a constant containing several of the constants discussed in the previous section, and \( a, m \) and \( n \) are positive integers. The integration indicated above is easily carried out to give

\[ W_{ij} = -c \lambda^{m+a} (z \lambda + y_i)^R \left\{ \frac{R^n}{2 \lambda + y_i} + \frac{n R^{n-1}}{(2 \lambda + y_i)^2} + \frac{n(n-1) R^{n-2}}{(2 \lambda + y_i)^3} \right\} + \cdots + \frac{n! R}{(2 \lambda + y_i)^n} + \frac{n!}{(2 \lambda + y_i)^{n+1}} \]

Consider only the first of the two terms; this can be rewritten

\[ W_{ij}^{(1)} = -c \lambda^{m+a} (z \lambda + y_i)^R \left\{ \frac{(2 \lambda + y_i)^n R^h + (2 \lambda + y_i)^{n-1} n R^{n-1}}{(2 \lambda + y_i)^{n+1}} + \frac{(2 \lambda + y_i)^{n-2} n(n-1) R^{n-2}}{n! + n!} \right\}

Call the polynomial inside the brackets \( P \). Then

\[ \frac{\partial W_{ij}^{(1)}}{\partial \lambda} = \\left\{ \frac{m+a}{\lambda} \right\} W_{ij}^{(1)} - C \lambda^{m+a} e^{-(z \lambda + y_i) R} \frac{P}{(2 \lambda + y_i)^{n+1}} \right\} \frac{\partial P}{\partial \lambda}, \]

\[ \frac{\partial P}{\partial \lambda} = \frac{2 P_1}{2 \lambda + y_i}, \]

where \( P_1 \) is obtained from \( P \) by multiplying each term of \( P \) by the power of \( R \) present in that term. Represent the power by \( p \); then
\[
\frac{\partial W_{i,j}^{(u)}}{\partial \lambda} = \left\{ \frac{m+a}{\lambda} - 2R - \frac{2(n+1-\phi)}{2\lambda+Y_i} \right\} W_{i,j}^{(u)} ; \\
\phi = n, n-1, n-2, \ldots, 1, \sigma.
\]

Let \( n+1 - \phi = \ell. \)

Finally,
\[
\frac{\partial W_{i,j}^{(1)}}{\partial \lambda} = \left\{ \frac{m+a}{\lambda} - 2R - \frac{2\ell}{2\lambda+Y_i} \right\} W_{i,j}^{(1)} ; \\
\ell = 1, 2, 3, \ldots, n, n+1.
\]

\[
\left\{ \frac{m+a}{\lambda} - 2R - \frac{2\ell}{2\lambda+Y_i} \right\} P = \\
(2\lambda+Y_i)^n \left\{ R^n \left( \frac{m+a}{\lambda} - 2R \right) \right\} \\
+ (2\lambda+Y_i)^{n-1} \left\{ R^{n-1}(-2) + n R^{n-1} \left( \frac{m+a}{\lambda} - 2R \right) \right\} \\
+ (2\lambda+Y_i)^{n-2} \left\{ n R^{n-2}(-4) + n(n-1) R^{n-2} \left( \frac{m+a}{\lambda} - 2R \right) \right\} \\
+ \cdots + (2\lambda+Y_i) \left\{ \frac{n!}{2} R^{2}(-2)(n-1) + n! R \left( \frac{m+a}{\lambda} - 2R \right) \right\} \\
+ \left\{ n! R(-2n) + n! \left( \frac{m+a}{\lambda} - 2R \right) \right\}.
\]
Admittedly, the equation for the derivative does not look particularly simple in this form. There are a number of features, not immediately apparent, perhaps, which make this formulation quite easy to use. It is to be noticed that each term in the original integration—only one is considered here—leads to a polynomial in \( \lambda R / (2 \lambda + Y) \), the coefficient of each term containing 2 powers of \( \lambda R \). The coefficients of the powers of \( \lambda R \) are extremely simple to compute, since each derives from the previous one in a simple way. This in itself saves considerable time. In general, the constant \( C \) can be factored into the product of two constants, \( C'N \), where \( C' \) is
a constant, again containing several other constants, and $N$ is an integer. The advantage of the factoring lies in this; each integral contains a series of terms, of which only the $j$-th was considered here, with the same value for $C'$, but different values of $N$, the same value of $a$, and values of $m$ and $n$ that increase by one from one term to the next. Thus $C'$ can be factored outside the integral. Now it is quite a simple matter to build a rectangular array, with powers of $\frac{\lambda}{(2 \lambda + Y)}$ on one axis and powers of $\lambda R$ on the other, and then enter the various coefficients at the intersection of the proper row and column. This is done for each term in the integral; then the entire array is summed up to get the polynomial coefficients of the polynomial.

This can be done for the other integral type with a similar procedure, so the entire derivative can be constructed in very little time. Formulas can be derived by a similar method for the energy expression as well, but little or no time is saved here. In this work all equations have been derived by both this method and the direct one to minimize the chance of error.
IV. DISCUSSION

It is impossible to judge the validity of the proposed models on the basis of the results of Chapter III. Certainly the results do not favor one set of models over the other. But, neither can it be said that they weaken the arguments for both sets of models. The question must remain unresolved until further improvements are incorporated into the calculations. It does seem, however, that the agreement of the calculated and experimental values in order of magnitude is support for the general model of a Z center—an alkaline earth cation, with or without associated vacancies or vacancy aggregates, plus one or two trapped electrons.

Perhaps the biggest surprise is the large difference in the calculated ground state energies of Ca$^+$ and Sr$^+$. The origin of this discrepancy is clarified somewhat by using the potential function of the last chapter to estimate the ionization potentials of these two ions in vacuum. These results are then compared with the empirical values.

The potential energy is

$$V = \left( B \frac{V^2}{R^2} - 1 \right) \frac{Z}{r} \sum_{i=1}^{4} \left( e_i \frac{Q^{-V_i}}{r} \right) - V_0, \quad 0 \leq r \leq R,$$

and

$$V = -\frac{2}{r}, \quad R \leq r \leq \infty,$$

where $V_0$ now is $2/R$, but the rest of the symbols retain their previous meaning. The same ground state trial wave functions are used in the
same variational procedure. The results are \(-13.099\) ev and \(-18.729\) ev for Ca\(^+\) and Sr\(^+\), respectively, and the corresponding experimental results are \(-11.871\) ev and \(-11.023\) ev, respectively (11, p. 30, 36). Thus the Ca\(^+\) result is off about 10\% and the Sr\(^+\) about 70\%.

It is not clear just why the Sr\(^+\) result should be so much worse than the Ca\(^+\) when exactly the same approach was used for each. A priori it might be expected that Sr\(^+\) would give the better result since the statistical method gains validity as the atomic number increases. Two significant differences are noticed when Sr\(^+\) is compared with Ca\(^+\). First, the potential energy becomes nearly twice as deep very close to the nucleus. Second, this is compensated for by the increased principal quantum number of the trapped-electron wave function. The attraction of the nucleus is greater, but the exclusion principle forces the electron farther from the nucleus. It seems these two should nearly cancel one another; in fact the latter should even predominate slightly. In the present calculations, however, the former effect seems to outweigh the latter to an appreciable extent. To obtain better results, then, will certainly require the use of a more precise potential function and perhaps more flexible trial wave functions.

When the calculations for a substitutional distributed charge were discussed, it was pointed out that the addition of an empirical correction term, which raised the vacuum-case ground state 5.38 ev to equate it to the empirical result, raised the crystal-case ground state 3.17 ev. In other words, the ground state in the crystal was
raised about 60% of the error in the calculated ground state in vacuum. If this same percentage is assumed applicable—it must be admitted that there is no justification for this assumption—to the vacuum results mentioned in this chapter, then the ground state in the crystal is raised about 0.7 eV for Ca\(^{+}\) and 4.6 eV for Sr\(^{+}\). Thus the ground state values of Ca\(^{+}\) in the crystals studied would be about \(-3.1\) to \(-3.4\) eV, and of Sr\(^{+}\), about \(-4.2\) to \(-4.5\) eV. This result supports the idea that the difference in the calculated ground state energies is not real, but is due to an imprecise potential function for Sr\(^{+}\). If the difference were real, it would be interesting to speculate that corresponding bands of strontium-doped and calcium-doped crystals originated in two different kinds of center; but, based on these results, such a concept must be considered highly speculative indeed.
BIBLIOGRAPHY


### APPENDIX I

**CONSTANTS USED IN COMPUTATIONS AND THEIR SOURCES**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Magnitude</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Radius</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.94 A</td>
<td>15, p. 81</td>
</tr>
<tr>
<td>Sr&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>1.10 A</td>
<td>15, p. 81</td>
</tr>
<tr>
<td><strong>Dielectric constant (static)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>4.85</td>
<td>12, p. 445</td>
</tr>
<tr>
<td>NaC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>5.87</td>
<td>12, p. 445</td>
</tr>
<tr>
<td>KC&lt;sub&gt;1&lt;/sub&gt;*</td>
<td>4.68</td>
<td>20, p. 12</td>
</tr>
<tr>
<td>NaC&lt;sub&gt;1&lt;/sub&gt;*</td>
<td>5.62</td>
<td>20, p. 12</td>
</tr>
<tr>
<td><strong>Dielectric constant (high-frequency)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2.13</td>
<td>20, p. 12</td>
</tr>
<tr>
<td>NaC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2.25</td>
<td>20, p. 12</td>
</tr>
<tr>
<td><strong>Lattice parameter</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>6.2931 A</td>
<td>ASTM x-ray data cards</td>
</tr>
<tr>
<td>NaC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>5.6402 A</td>
<td></td>
</tr>
<tr>
<td><strong>Madelung constant</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaC&lt;sub&gt;1&lt;/sub&gt;-type lattice</td>
<td>1.747558</td>
<td>27, p. 107</td>
</tr>
<tr>
<td><strong>Polarizability</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.179 A&lt;sup&gt;3&lt;/sup&gt;</td>
<td>20, p. 14</td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.83 A&lt;sup&gt;3&lt;/sup&gt;</td>
<td>20, p. 14</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.47 A&lt;sup&gt;3&lt;/sup&gt;</td>
<td>20, p. 14</td>
</tr>
<tr>
<td>Sr&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.86 A&lt;sup&gt;3&lt;/sup&gt;</td>
<td>20, p. 14</td>
</tr>
<tr>
<td><strong>Volume per ion pair</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>61.86 A&lt;sup&gt;3&lt;/sup&gt;</td>
<td>31, p. 891</td>
</tr>
<tr>
<td>NaC&lt;sub&gt;1&lt;/sub&gt;</td>
<td>44.58 A&lt;sup&gt;3&lt;/sup&gt;</td>
<td>31, p. 891</td>
</tr>
<tr>
<td><strong>First Bohr radius of hydrogen atom</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.529172 A</td>
<td>5, p. 268</td>
</tr>
<tr>
<td><strong>Hydrogen atom ionization potential</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.59765 ev</td>
<td>5, p. 270</td>
</tr>
<tr>
<td><strong>Energy conversion factor,</strong> wave numbers to electron volts</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0001239767 ev cm</td>
<td>5, p. 270</td>
</tr>
</tbody>
</table>

*These were used in the substitutional point charge calculations and in the calculations based on the artificial potential function.*
APPENDIX II

POLYNOMIAL COEFFICIENTS

The polynomial coefficients (all divided by 100) have been typed directly from the tapes used to store them in the computer memory. The symbolism used to identify the various sets is \((p,n_l)\); \(p\) is the subscript of \(P\) in the original equations, and \(n\) and \(l\) are the principal and azimuthal quantum numbers of the particular quantum state. The coefficients are always given in decreasing order of the power of the variable. For polynomials 1, 2, 8, and 9, there is one line for each value of the index \(k\), with the maximum value of \(k\) being given first and the others following in descending order.
<table>
<thead>
<tr>
<th>(1,50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-38320128</td>
</tr>
<tr>
<td>-38320128 81430272</td>
</tr>
<tr>
<td>-19160064 81430272 -75479040</td>
</tr>
<tr>
<td>-6386688 40715136 -75479040 40061952</td>
</tr>
<tr>
<td>-1596672 13571712 -37739520 40061952 -13402368</td>
</tr>
<tr>
<td>-319334.4 3392928 -125798140 20030976 -13402368 2924208</td>
</tr>
<tr>
<td>-53222.4 675385.6 -3144960 6676992 -670118 2924208 -414720</td>
</tr>
<tr>
<td>-7603.2 113097.6 -628992 16692148 -2233728 290881460.8 -131402368</td>
</tr>
<tr>
<td>-950.4 16156.8 -104632 333849.6 -558482 487388 -207360 36720 -1836</td>
</tr>
<tr>
<td>-105.6 2019.6 -14376 55641.6 -111686.4 121842 -69120 18360 -1836 40.5</td>
</tr>
<tr>
<td>-10.56 224.4 -1872 7948.8 -18616.4 24368.4 -17280 6120 -918 40.5 0</td>
</tr>
<tr>
<td>-.96 22.44 -208 993.6 -2659.2 4061.4 -3456 1530 -306 20.25 0 0</td>
</tr>
<tr>
<td>-0.08 2.04 -20.8 110.4 -332.4 580.2 -576 306 -76.5 6.75 0 0 0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(1,51)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-38320128</td>
</tr>
<tr>
<td>-38320128 75043584</td>
</tr>
<tr>
<td>-19160064 75043584 -62705664</td>
</tr>
<tr>
<td>-6386688 37521792 -62705664 29088460.8</td>
</tr>
<tr>
<td>-1596672 12507264 -3132832 29088460.8 -8116416</td>
</tr>
<tr>
<td>-319334.4 3166316 -10450944 14544230.4 -8116416 1367604</td>
</tr>
<tr>
<td>-53222.4 625363.2 -261736 4848076.8 -4058208 1367604 -129600</td>
</tr>
<tr>
<td>-7603.2 104227.2 -522547.2 1212019.2 -1352736 683802 -129600 5400</td>
</tr>
<tr>
<td>-950.4 14839.6 -87091.2 242403.84 -338184 227934 -64800 5400 0</td>
</tr>
<tr>
<td>-105.6 1861.2 -12641.6 40400.64 -67636.8 56983.5 -21600 2700 0 0</td>
</tr>
<tr>
<td>-10.56 206.8 -1555.2 5771.52 -11272.8 11396.7 -5400 900 0 0 0</td>
</tr>
<tr>
<td>-.96 20.68 -172.8 721.44 -1610.4 1899.45 -1080 225 0 0 0</td>
</tr>
<tr>
<td>-0.08 1.88 -17.28 80.16 -201.3 271.35 -180 45 0 0 0 0 0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(1,42)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-72576</td>
</tr>
<tr>
<td>-72576 76204.8</td>
</tr>
<tr>
<td>-36288 76204.8 -26611.2</td>
</tr>
<tr>
<td>-12096 38102.4 -26611.2 3175.2</td>
</tr>
<tr>
<td>-3024 12700.8 -13305.6 3175.2 0</td>
</tr>
<tr>
<td>-604.8 3175.2 -4435.2 1597.6 0 0</td>
</tr>
<tr>
<td>-100.8 635.04 -1108.8 529.2 0 0 0</td>
</tr>
<tr>
<td>-14.4 105.84 -221.76 132.3 0 0 0 0</td>
</tr>
<tr>
<td>-1.8 15.12 -36.96 26.46 0 0 0 0 0 0</td>
</tr>
<tr>
<td>-.2 1.89 -5.28 4.41 0 0 0 0 0 0</td>
</tr>
<tr>
<td>-.02 0.21 -.66 .63 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(1,40)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-72576</td>
</tr>
<tr>
<td>-72576 119750.4</td>
</tr>
<tr>
<td>-36288 119750.4 -82252.8</td>
</tr>
<tr>
<td>-12096 59875.2 -82252.8 30542.4</td>
</tr>
<tr>
<td>-3024 19958.4 -41126.4 30542.4 -6609.6</td>
</tr>
<tr>
<td>-604.8 4989.6 -13708.8 15271.2 -6609.6 831.6</td>
</tr>
<tr>
<td>100.8 997.92 -3427.2 5090.4 -3304.8 831.6 -56.16</td>
</tr>
<tr>
<td>-14.4 166.32 -685.44 1272.6 -1101.6 415.8 -56.16 1.62</td>
</tr>
<tr>
<td>-1.8 23.76 -114.24 254.52 -275.4 138.6 -28.08 1.62 0</td>
</tr>
<tr>
<td>-.2 2.97 -16.32 42.42 -55.08 34.65 -9.36 .81 0 0</td>
</tr>
<tr>
<td>-.02 .33 -2.04 6.06 -9.18 6.93 -2.34 .27 0 0 0</td>
</tr>
<tr>
<td>(1,41)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-72576</td>
</tr>
<tr>
<td>-72576 105235.2</td>
</tr>
<tr>
<td>-36288 105235.2 -60480</td>
</tr>
<tr>
<td>-12096 52617.6 -60480 17388</td>
</tr>
<tr>
<td>-3024 17539.2 -30240 17388 -2520</td>
</tr>
<tr>
<td>-604.8 4384.8 -10080 8694 -2520 150</td>
</tr>
<tr>
<td>100.8 876.96 -2520 2890 -1260 150 0</td>
</tr>
<tr>
<td>-14.4 146.16 -504 724.5 -420 75 0 0</td>
</tr>
<tr>
<td>-1.8 20.88 -84 144.9 -105 25 0 0 0</td>
</tr>
<tr>
<td>-.2 2.61 -12 24.15 -21 6.25 0 0 0 0</td>
</tr>
<tr>
<td>-.02 .29 -1.5 3.45 -3.5 1.25 0 0 0 0 0</td>
</tr>
<tr>
<td>(1,32)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-806.4</td>
</tr>
<tr>
<td>-806.4 352.8</td>
</tr>
<tr>
<td>-403.2 352.8 0</td>
</tr>
<tr>
<td>-134.4 176.4 0 0</td>
</tr>
<tr>
<td>-33.6 58.8 0 0 0</td>
</tr>
<tr>
<td>-6.72 14.7 0 0 0 0</td>
</tr>
<tr>
<td>-1.12 2.94 0 0 0 0 0</td>
</tr>
<tr>
<td>-.16 .49 0 0 0 0 0 0</td>
</tr>
<tr>
<td>-.02 .07 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td>(2,50)</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>-290304</td>
</tr>
<tr>
<td>-290304</td>
</tr>
<tr>
<td>-145152</td>
</tr>
<tr>
<td>-48384</td>
</tr>
<tr>
<td>-12096</td>
</tr>
<tr>
<td>-2415.2</td>
</tr>
<tr>
<td>-403.2</td>
</tr>
<tr>
<td>-57.6</td>
</tr>
<tr>
<td>-7.2</td>
</tr>
<tr>
<td>-8</td>
</tr>
<tr>
<td>-.08</td>
</tr>
<tr>
<td>(2,51)</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>-290304</td>
</tr>
<tr>
<td>-290304</td>
</tr>
<tr>
<td>-145152</td>
</tr>
<tr>
<td>-48384</td>
</tr>
<tr>
<td>-12096</td>
</tr>
<tr>
<td>-2419.2</td>
</tr>
<tr>
<td>-403.2</td>
</tr>
<tr>
<td>-57.6</td>
</tr>
<tr>
<td>-7.2</td>
</tr>
<tr>
<td>-.08</td>
</tr>
<tr>
<td>(2,42)</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>-806.4</td>
</tr>
<tr>
<td>-806.4</td>
</tr>
<tr>
<td>-403.2</td>
</tr>
<tr>
<td>-134.4</td>
</tr>
<tr>
<td>-33.6</td>
</tr>
<tr>
<td>-6.72</td>
</tr>
<tr>
<td>-1.12</td>
</tr>
<tr>
<td>-.16</td>
</tr>
<tr>
<td>-.02</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>
(2,40)

-806.4
-806.4 1663.2
-403.2 1663.2 -1468.8
-134.4 831.6 -1468.8 727.2
-33.6 277.2 -734.4 727.2 -220.32
-6.72 69.3 -244.8 363.6 -220.32 41.58
-1.12 13.86 -61.2 121.2 -110.16 41.58 -4.68
-.16 2.31 -12.24 30.3 -36.72 20.79 -4.68 .27
-.02 .33 -2.04 6.06 -9.18 6.93 -2.34 .27 0

(2,41)

-806.4
-806.4 1461.6
-403.2 1461.6 -1080
-134.4 730.8 -1080 414
-33.6 243.6 -540 414 -84
-6.72 60.9 -180 207 -84 7.5
-1.12 12.18 -45 69 -42 7.5 0
-.16 2.03 -9 17.25 -14 3.75 0 0
-.02 .29 -1.5 3.45 -3.5 1.25 0 0 0

(2,32)

-14.4
-14.4 8.4
-7.2 8.4 0
-2.4 4.2 0 0
-.6 1.4 0 0 0
-.12 .35 0 0 0 0
-.02 .07 0 0 0 0 0
<table>
<thead>
<tr>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
<th>Column 5</th>
<th>Column 6</th>
<th>Column 7</th>
<th>Column 8</th>
<th>Column 9</th>
<th>Column 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,50</td>
<td>-38320128</td>
<td>81430272</td>
<td>-75479040</td>
<td>400611952</td>
<td>-13402368</td>
<td>2924208</td>
<td>-4114720</td>
<td>36720</td>
<td>-1836</td>
</tr>
<tr>
<td>3,51</td>
<td>-38320128</td>
<td>75043584</td>
<td>-62705664</td>
<td>29088460.8</td>
<td>-8116416</td>
<td>1367604</td>
<td>-129600</td>
<td>5400</td>
<td>0</td>
</tr>
<tr>
<td>3,42</td>
<td>-72576</td>
<td>76204.8</td>
<td>-26611.2</td>
<td>3175.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3,40</td>
<td>-72576</td>
<td>119750.4</td>
<td>-82252.8</td>
<td>30542.4</td>
<td>-6609.6</td>
<td>831.6</td>
<td>-56.16</td>
<td>1.62</td>
<td>0</td>
</tr>
<tr>
<td>3,41</td>
<td>-72576</td>
<td>105235.2</td>
<td>-60480</td>
<td>17388</td>
<td>-2520</td>
<td>150</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3,32</td>
<td>-806.4</td>
<td>352.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4,50</td>
<td>-290304</td>
<td>740275.2</td>
<td>-838656</td>
<td>556416</td>
<td>-239328</td>
<td>69624</td>
<td>-13824</td>
<td>1836</td>
<td>-153</td>
</tr>
<tr>
<td>4,51</td>
<td>-290304</td>
<td>682214.4</td>
<td>-696729.6</td>
<td>404006.4</td>
<td>-144936</td>
<td>32562</td>
<td>-4320</td>
<td>270</td>
<td>0</td>
</tr>
<tr>
<td>4,42</td>
<td>-806.4</td>
<td>1058.4</td>
<td>-475.2</td>
<td>75.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4,40</td>
<td>-806.4</td>
<td>1663.2</td>
<td>-1468.8</td>
<td>727.2</td>
<td>-220.32</td>
<td>41.58</td>
<td>-4.68</td>
<td>.27</td>
<td>0</td>
</tr>
<tr>
<td>4,41</td>
<td>-806.4</td>
<td>1461.6</td>
<td>-1080</td>
<td>414</td>
<td>-84</td>
<td>7.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4,32</td>
<td>-14.4</td>
<td>8.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(5,50)</td>
<td>0.16</td>
<td>-3.2</td>
<td>25.6</td>
<td>-105.6</td>
<td>242.4</td>
<td>-312</td>
<td>216</td>
<td>-72</td>
<td>9</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>--------</td>
<td>-------</td>
<td>------</td>
<td>------</td>
<td>-----</td>
<td>---</td>
</tr>
<tr>
<td>(5,51)</td>
<td>0.32</td>
<td>-5.76</td>
<td>40.32</td>
<td>-139.2</td>
<td>248.4</td>
<td>-216</td>
<td>72</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(5,42)</td>
<td>0.04</td>
<td>-0.24</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(5,40)</td>
<td>0.04</td>
<td>-0.48</td>
<td>2.16</td>
<td>-4.56</td>
<td>4.68</td>
<td>-2.16</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(5,41)</td>
<td>0.04</td>
<td>-0.4</td>
<td>1.4</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(5,32)</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

| (6,50) | -0.16 | 3.28 | -26.84 | 113.44 | -267.76 | 357.12 | -259.2 | 93.6 | -12.6 | 9 | 0.45 |
| (6,51) | -0.32 | 5.92 | -42.48 | 150.72 | -277.68 | 252.36 | -89.1 | 1.8 | 2.7 | 2.7 | 1.35 |
| (6,42) | -0.16 | 1.04 | -1.64 | 0.12 | 3 | 6 | 9 | 9 | 0.45 |
| (6,40) | -0.16 | 2 | -9.32 | 20.52 | -22.14 | 11.16 | -1.98 | 0.18 | 0.09 |
| (6,41) | -0.16 | 1.68 | -6.12 | 9.24 | -4.9 | 0.2 | 3 | 3 | 0.15 |
| (6,32) | -0.08 | 0.04 | 1 | 2 | 3 | 3 | 0.15 |

| (7,50) | -0.16 | 3.36 | -28.16 | 122.24 | -298.08 | 415.2 | -321.6 | 129.6 | -23.4 | 1.8 | 0 |
| (7,51) | -0.32 | 6.08 | -44.8 | 163.84 | -313.68 | 301.2 | -117.6 | 3.6 | 3.6 | 1.8 | 0 |
| (7,42) | -0.04 | 0.28 | -0.48 | 0.06 | 0.12 | 0.18 | 0.18 | 0.09 | 0 |
| (7,40) | -0.04 | 0.52 | -2.52 | 5.82 | -6.72 | 3.78 | -0.9 | 0.09 | 0 |
| (7,41) | -0.04 | 0.44 | -1.68 | 2.7 | -1.6 | 0.1 | 0.05 | 0 |
| (7,32) | -0.08 | 0.08 | 1.16 | 0.24 | 0.24 | 0.12 | 0 |
(8,50)

1596672
1596672 -2903040
798336 -2903040 2322432
266112 -1451520 2322432 -1064448
66528 -483840 1161216 -1064448 305424
13305.6 -120960 387072 -532224 305424 -56160
2217.6 -24192 96768 -177408 152712 -56160 6480
316.8 -4032 19353.6 -44352 50904 -28080 6480 -432
39.6 -76 3225.6 -8870.4 12726 -9360 3240 -432 13.5
4.4 -72 460.8 -1478.4 2545.2 -2340 1080 -216 13.5 0
.44 -8 57.6 -211.2 424.2 -468 270 -72 6.75 0 0
.04 -8 6.4 -26.4 60.6 -78 54 -18 2.25 0 0 0

(8,51)

1596672
1596672 -2612736
798336 -2612736 1828915.2
266112 -1306368 1828915.2 -701568
66528 -435456 914457.6 -701568 156492
13305.6 -108864 304819.2 -350784 156492 -194440
2217.6 -21772.8 76204.8 -116928 78246 -194440 1080
316.8 -3628.8 15240.96 -29232 26082 -9720 1080 0
39.6 -518.4 2540.16 -5846.4 6520.5 -3240 540 0 0
4.4 -64.8 362.88 -974.4 1304.1 -810 180 0 0 0
.44 -7.2 45.36 -139.2 217.35 -162 45 0 0 0 0
.04 -7.2 5.04 -17.4 31.05 -27 9 0 0 0 0

(8,42)

3628.8
3628.8 -2419.2
1814.4 -2419.2 453.6
604.8 -1209.6 453.6 0
151.2 -403.2 226.8 0 0
30.24 -100.8 75.6 0 0 0
5.04 -20.16 18.9 0 0 0 0
.72 -3.36 3.78 0 0 0 0 0
.09 -.48 .63 0 0 0 0 0
.01 -.06 0.09 0 0 0 0 0
(8,40)

<table>
<thead>
<tr>
<th>3628.8</th>
<th>3628.8</th>
<th>4838.4</th>
<th>3628.8</th>
<th>3628.8</th>
<th>4838.4</th>
<th>2721.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1814.4</td>
<td>1814.4</td>
<td>4838.4</td>
<td>2721.6</td>
<td>620.8</td>
<td>620.8</td>
<td>-820.8</td>
</tr>
<tr>
<td>151.2</td>
<td>151.2</td>
<td>1360.8</td>
<td>140.4</td>
<td>140.4</td>
<td>-12.96</td>
<td>-12.96</td>
</tr>
<tr>
<td>30.24</td>
<td>-201.6</td>
<td>453.6</td>
<td>-410.4</td>
<td>140.4</td>
<td>-12.96</td>
<td>5.04</td>
</tr>
<tr>
<td>0.04</td>
<td>-40.32</td>
<td>113.4</td>
<td>-136.8</td>
<td>70.2</td>
<td>-12.96</td>
<td>.54</td>
</tr>
<tr>
<td>.72</td>
<td>-6.72</td>
<td>22.68</td>
<td>-34.2</td>
<td>23.4</td>
<td>-6.48</td>
<td>.54</td>
</tr>
<tr>
<td>.09</td>
<td>-.96</td>
<td>3.78</td>
<td>-6.84</td>
<td>5.85</td>
<td>-2.16</td>
<td>.27</td>
</tr>
<tr>
<td>.01</td>
<td>-.12</td>
<td>.54</td>
<td>-1.14</td>
<td>1.17</td>
<td>-.54</td>
<td>.09</td>
</tr>
</tbody>
</table>

(8,41)

<table>
<thead>
<tr>
<th>3628.8</th>
<th>3628.8</th>
<th>4032</th>
</tr>
</thead>
<tbody>
<tr>
<td>1814.4</td>
<td>1814.4</td>
<td>4032</td>
</tr>
<tr>
<td>620.8</td>
<td>620.8</td>
<td>1764</td>
</tr>
<tr>
<td>151.2</td>
<td>-672</td>
<td>1764</td>
</tr>
<tr>
<td>30.24</td>
<td>-168</td>
<td>-360</td>
</tr>
<tr>
<td>5.04</td>
<td>-33.6</td>
<td>73.5</td>
</tr>
<tr>
<td>.72</td>
<td>-.8</td>
<td>2.45</td>
</tr>
<tr>
<td>.09</td>
<td>-.8</td>
<td>2.45</td>
</tr>
<tr>
<td>.01</td>
<td>-.1</td>
<td>.35</td>
</tr>
</tbody>
</table>

(8,32)

<table>
<thead>
<tr>
<th>50.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.4</td>
</tr>
<tr>
<td>25.2</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>2.1</td>
</tr>
<tr>
<td>8.4</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>.42</td>
</tr>
<tr>
<td>.07</td>
</tr>
<tr>
<td>.01</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>7257.6</td>
</tr>
<tr>
<td>2419.2</td>
</tr>
<tr>
<td>604.8</td>
</tr>
<tr>
<td>120.96</td>
</tr>
<tr>
<td>20.16</td>
</tr>
<tr>
<td>2.88</td>
</tr>
<tr>
<td>.36</td>
</tr>
<tr>
<td>.04</td>
</tr>
</tbody>
</table>

\[7257.6 - 32256 + 32256 - 19008 = 0.0\]

\[[9,50]\]

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>7257.6</td>
<td>29030.4</td>
<td>25401.6</td>
<td>12528</td>
<td></td>
</tr>
<tr>
<td>2419.2</td>
<td>-14515.2</td>
<td>25401.6</td>
<td>-12528</td>
<td></td>
</tr>
<tr>
<td>604.8</td>
<td>-4838.4</td>
<td>12700.8</td>
<td>-12528</td>
<td></td>
</tr>
<tr>
<td>120.96</td>
<td>-1209.6</td>
<td>4233.6</td>
<td>-6264</td>
<td></td>
</tr>
<tr>
<td>20.16</td>
<td>-241.92</td>
<td>1058.4</td>
<td>-2088</td>
<td></td>
</tr>
<tr>
<td>2.88</td>
<td>-40.32</td>
<td>211.68</td>
<td>-522</td>
<td></td>
</tr>
<tr>
<td>.36</td>
<td>-5.76</td>
<td>35.28</td>
<td>-104.4</td>
<td></td>
</tr>
<tr>
<td>.04</td>
<td>-7.2</td>
<td>5.04</td>
<td>-17.4</td>
<td></td>
</tr>
</tbody>
</table>

\[7257.6 - 29030.4 + 25401.6 - 12528 = 0.0\]

\[[9,51]\]

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50.4</td>
<td>-43.2</td>
<td>25.2</td>
<td>-43.2</td>
<td>10.8</td>
</tr>
<tr>
<td>8.4</td>
<td>-21.6</td>
<td>10.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.1</td>
<td>-7.2</td>
<td>5.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>.42</td>
<td>-1.8</td>
<td>1.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>.07</td>
<td>-.36</td>
<td>.45</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>.01</td>
<td>-.06</td>
<td>.09</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\[50.4 - 43.2 + 25.2 - 43.2 + 10.8 = 0.0\]

\[[9,42]\]
\begin{align}
\begin{array}{cccc}
50.4 & -86.4 & 25.2 & -86.4 64.8 \\
8.4 & -43.2 & 64.8 & -27.36 \\
2.1 & -14.4 & 32.4 & -27.36 7.02 \\
.42 & -3.6 & 10.8 & -13.68 7.02 -1.08 \\
.07 & -.72 & 2.7 & -4.56 3.51 -1.08 .09 \\
.01 & -.12 & .54 & -1.14 1.17 -.54 .09 0 \\
\end{array}
\end{align}
<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(12,50)</td>
<td>.08</td>
<td>-1.2</td>
<td>7.4</td>
<td>-23.2</td>
<td>40</td>
<td>-36</td>
<td>18</td>
</tr>
<tr>
<td>(12,51)</td>
<td>.16</td>
<td>-2.08</td>
<td>10.8</td>
<td>-26.4</td>
<td>31.8</td>
<td>-12.6</td>
<td>4.5</td>
</tr>
<tr>
<td>(12,42)</td>
<td>.02</td>
<td>-.04</td>
<td>.04</td>
<td>.12</td>
<td>.3</td>
<td>.6</td>
<td>.9</td>
</tr>
<tr>
<td>(12,40)</td>
<td>.02</td>
<td>-1.16</td>
<td>.52</td>
<td>-72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(12,41)</td>
<td>.02</td>
<td>-1.12</td>
<td>.28</td>
<td>-1.6</td>
<td>1.2</td>
<td>3</td>
<td>.3</td>
</tr>
<tr>
<td>(12,32)</td>
<td>.04</td>
<td>.12</td>
<td>.3</td>
<td>.6</td>
<td>.9</td>
<td>.9</td>
<td>.45</td>
</tr>
<tr>
<td>(13,50)</td>
<td>.08</td>
<td>-1.24</td>
<td>7.84</td>
<td>-25.36</td>
<td>45.12</td>
<td>-43.2</td>
<td>21.6</td>
</tr>
<tr>
<td>(13,51)</td>
<td>.16</td>
<td>-2.16</td>
<td>11.52</td>
<td>-29.28</td>
<td>36.36</td>
<td>-17.1</td>
<td>1.8</td>
</tr>
<tr>
<td>(13,42)</td>
<td>.08</td>
<td>-2.12</td>
<td>.3</td>
<td>.6</td>
<td>.9</td>
<td>.9</td>
<td>.45</td>
</tr>
<tr>
<td>(13,40)</td>
<td>.08</td>
<td>-1.68</td>
<td>2.28</td>
<td>-3.42</td>
<td>2.52</td>
<td>.54</td>
<td>.18</td>
</tr>
<tr>
<td>(13,41)</td>
<td>.08</td>
<td>-1.52</td>
<td>1.24</td>
<td>-.9</td>
<td>2</td>
<td>.3</td>
<td>.3</td>
</tr>
<tr>
<td>(13,32)</td>
<td>.04</td>
<td>.1</td>
<td>.2</td>
<td>.3</td>
<td>.3</td>
<td>.15</td>
<td></td>
</tr>
<tr>
<td>(14,50)</td>
<td>.08</td>
<td>-1.28</td>
<td>8.32</td>
<td>-27.84</td>
<td>51.6</td>
<td>-52.8</td>
<td>28.8</td>
</tr>
<tr>
<td>(14,51)</td>
<td>.16</td>
<td>-2.24</td>
<td>12.32</td>
<td>-32.64</td>
<td>42.6</td>
<td>-22.8</td>
<td>1.8</td>
</tr>
<tr>
<td>(14,42)</td>
<td>.04</td>
<td>-1.12</td>
<td>.06</td>
<td>.12</td>
<td>.18</td>
<td>.18</td>
<td>.09</td>
</tr>
<tr>
<td>(14,40)</td>
<td>.04</td>
<td>-1.36</td>
<td>1.26</td>
<td>-2.04</td>
<td>1.62</td>
<td>-.54</td>
<td>.09</td>
</tr>
<tr>
<td>(14,41)</td>
<td>.04</td>
<td>-1.28</td>
<td>.7</td>
<td>-.6</td>
<td>1</td>
<td>.1</td>
<td>.05</td>
</tr>
<tr>
<td>(14,32)</td>
<td>.04</td>
<td>.08</td>
<td>.12</td>
<td>.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>