1978

Studies of Excess Electrons in Molten Alkali Halides.

Clarence William Finley Jr
Louisiana State University and Agricultural & Mechanical College

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STUDIES OF EXCESS ELECTRONS IN MOLTEN ALKALI
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THE LOUISIANA STATE UNIVERSITY AND
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STUDIES OF EXCESS ELECTRONS
IN MOLTEN ALKALI HALIDES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Clarence William Finley, Jr.
B.A., California State College, 1964
December 1978
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During my education in the Department of Chemistry at Louisiana State University, I have received many incentives to persevere. Some of these incentives must be acknowledged.

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Chapter I is a review of the previous work on solvated electrons in polar and nonpolar media, and a cursory overview of the thermodynamics of fused salts.

In Chapter II, two approaches are developed to account for the major interactions that lead to a stable localized state for excess electrons in molten alkali halide melts. In both the \textit{ab initio} and the pseudopotential approach we assume that the excess electron is localized in a negative ion vacancy in the melt. We assume the nearest neighbors in the solvation cluster are the metal ions and the next nearest neighbors are halide ions. The coordination number and the size of this cluster are not determined by the initial trap, but are essentially determined by the interionic interactions and by the statistical mechanics of the melt including the extra electron.

At the \textit{a priori} level, a preliminary Hartree-Fock calculation was done on a small number of reasonably placed neighbors, and the minimum on the total energy surface was found with respect to a single parameter used to define the radius of the cluster or "cavity". An existing program, GAUSSIAN 70 (QCPE No. 236), modified to accept the floating orbitals, was used to calculate the total energy. The cluster \((\text{NaCl}_4)^-\), where the cations form a tetrahedron with the anions oriented so that the dipole vector points to the localization (cavity) center along the dipole-cavity center vector, was found to be stable. The cation-cavity center distance, \(R\), was found to be 2.35 \(\text{Å}\). The calculated \(1s - 2p\) transition, \(\hbar\nu\), for the solvated electron is 2.86
ev and the calculated solvation energy, $E_s$, is -4.38 ev.

Because such calculations are costly, a second, one-electron, approach was developed. The ion-ion interactions, assumed to be pairwise additive, are approximated by the Born-Mayer-Huggins potential. Pseudopotentials are used to calculate the cavity electron-ion contributions to the total energy. In addition, we have included a term, $V_0$, which represents part of the interaction of the solvated electron with the bulk melt. $V_0$ represents a sum of terms. One part is the long-range screened attractive polarization interactions and another part is the short-range repulsive interactions arising from exclusion forces. Furthermore, since $V_0$ is the energy of the non-localized (quasi-free) electronic state, and in this state the extra electron interacts with a large number of medium electrons, we assume that when the localized electron is far from the solvation cluster it interacts with the medium in this quasi-free manner.

The melts studied by this one-electron approach are NaCl, NaBr, KCl, KBr. The solvated state for the excess electron is found to be the most stable in these fused salts. The most stable cavity in each case is formed by a cluster with a tetrahedral geometry. For the most stable cavity the results are:

1) NaCl, $R = 2.70 \text{ Å}$, $h\nu = 2.36$ ev, $E_s = -2.53$ ev,
2) NaBr, $R = 2.79 \text{ Å}$, $h\nu = 2.27$ ev, $E_s = -2.59$ ev,
3) KCl, $R = 3.08 \text{ Å}$, $h\nu = 1.96$ ev, $E_s = -2.25$ ev,
4) KBr, $R = 3.14 \text{ Å}$, $h\nu = 1.91$ ev, $E_s = -2.31$ ev.

The advantage of the one-electron approach is that a large number
of configurations can be easily considered and the line shape can be calculated. Our line shape calculation includes the spherically symmetric vibrations of the anions with respect to the cations. These modes of vibration, weighted by the pair distribution function, produce a slight asymmetry of the line shape to the high energy side when these modes are included along with the radially symmetric "breathing" modes of the cavity. This accurate representation of the thermally accessible configurations gives a half-width of 30% of the absorption maximum for solvated electrons in molten KCl.
CHAPTER I

Previous Work on Excess Electrons in Fluids

"Curiouser and curiouser," said Alice in amazement at the White Rabbit's words and then hastily poured him another cup of tea so that he should not stop this exciting tale. Wiping his whiskers and paws very carefully the rabbit repeated grandly,

"Yes, quite an exciting discovery, in my opinion one whose impact still has to be explored. And the machines they used, you cannot imagine how complicated they were!"

"Yes, yes," stamped Alice a little impatiently, "but what did they discover?"

"Why the hydrated electron, of course."

"The what?"

Breathing heavily the White Rabbit pushed back his chair. "The hydrated electron."

"What is that? It sounds a very curious thing to be excited about."

"Ah—how can I describe it—A species older than homosapiens, a transient blueness when the lightning plays upon the rain..."

"That's all nonsense," interrupted Alice sharply, "you are making fun of me."

With a supercilious shrug the White Rabbit continued in his prosaic vein, "...the hydrated electron is an elusive phantom charge that's never still in its watery trap, so quick to react
that..."

"Gobbledygook!" retorted Alice, "I won't stand for these ridiculous ideas."

The White Rabbit stood up, gave her a quelling look and tucking his paws into his white coat returned to the laboratory. Over his shoulder came the mutterings... "What did she want me to say? That it is an excess electron bound in a self-induced stable quantum state of the polarized dielectric?"

"Well, that is a little clearer and a lot more logical," admitted Alice to herself as she began to clear away the cups and saucers.

Taken from Authors' Preface

by Geraldine A. Kenney
and David C. Walker

A. TIME-DEPENDENT ASPECTS

Many methods have been used for the creation of excess electrons in liquids, glasses, dense vapors and salt melts. The following is a list of some of those methods.

1. Injection from a photo-cathode immersed in a liquid.
2. Photoionization of solutes with a lower ionization potential than the solvent.
3. Ionization of the liquid or glass by high energy x-rays, γ-rays, or fast electrons.
4. Injection of electrons from semiconductor diodes by field emission from tips or sharp edges.
5. Injection of electrons from the vacuum or the gas phase into a liquid.
6. Periodic injection of electrons by AC-electrolysis from an electrode immersed in salt melts.
7. Dissolution of an alkali metal in a liquid to yield solvated electrons.

When excess electrons are introduced into a fluid there are many pathways for it to follow. Among these pathways are the following: 1) scavenging by impurities, 2) recombination with an ionized solvent molecule, 3) trapping by the container walls, 4) trapping by sites where a favorable trapping potential exists.

If an electron scavenger is present in a liquid with a concentration \([S_c]\) and, in the case where a homogeneous distribution of excess electrons is generated by a short pulse of radiation, the electron concentration is observed to decay exponentially with time. In such cases a pseudo-first-order rate constant \(k_{ap}\) is obtained. Variation of
 yields different values of $K_{ap}$ and the bimolecular rate constant $K_{sc}$ for the reaction

$$e^- + S_c \stackrel{K_{sc}}{\longrightarrow} S_c^-$$

is obtained. The rate of excess electron disappearance as a function of scavenger concentration is written as

$$-\frac{d[e^-]}{dt} = K_{sc} [S_c] [e^-] \quad \text{(1)}$$

with

$$K_{ap} = K_{sc} [S_c] \quad \text{(2)}$$

The plots of $K_{ap} \text{ vs } [S_c]$ are linear and hence $K_{sc}$ can be determined.

A list of good electron scavengers would include $SF_6$, $N_2O$, $O_2$, $CCl_4$, $C_2H_5Br$, $CH_3I$ and biphenyl.

Allen and Holroyd\(^1\) studied the recombination rates for n-pentane, n-hexane, and tetramethylysilane and concluded that the recombination rates are diffusion controlled and hence are proportional to the electron mobilities. They also determined $K_{sc}$ for several of the scavengers in the hydrocarbons mentioned and in several other nonpolar hydrocarbons. Characteristically $K_{sc}$ lies within an order of magnitude of $10^{-12} \text{ M}^{-1} \text{ S}^{-1}$ (reciprocal molar - reciprocal seconds) and are not diffusion controlled but can be correlated with $V_o$, the energy of a thermalized excess electron in its mobile state as determined from photoelectric threshold measurements.

The first three pathways are not of great interest in this study since they represent mechanisms whereby the objective of solvating an
excess electron is frustrated. There are time-dependent aspects of solvating an excess electron in a fluid which must be considered. When an extra electron is introduced into the fluid, for a short time afterwards (10^{-6} to 10^{-12} \text{s}^{-1}) the system exists in a non-equilibrium configuration. With time the fluid responds to the presence of the electron and the electron responds to the changing fluid configuration, i.e. the system relaxes. This point will be returned to later in this section. The final state of the electron and the final configuration of the fluid depend on the balance of forces in the system. The stability criteria will be discussed further in the next section.

The forces acting on the extra electron are usually separated into two categories for the purpose of discussion. According to this terminology they are "short" range and "long" range. Short-range forces arise from interactions between the extra electron and its nearest neighbors and possibly its next nearest neighbors. In the models that have been developed to describe the solvated electron short-range potentials fall off as r^{-n}, where n > 2 or as \exp(-\alpha r) for \alpha > 0, and long-range potentials fall off as r^{-1}.

The relative importance of these interactions depends heavily on the system under consideration. For example, in the discussion in section C on excess electron states in the low atomic number liquid rare gases we shall see that the dominate interactions are the short-range repulsions of the electron with the electrons in the liquid and give rise to a localized ground state for the electron. However, as the atomic number of the rare gas increases the long-range polarization interaction increases and leads to a dramatic change in the ground state of the electron.
As a further example of the relative importance of the inter­
actions in a fluid system, the discussion in section D will show that
both the short-range and the long-range interactions which arise due
to the permanent dipole of the solvent molecule can also lead to a
stable localized excess electron state.

In Chapter II the charge-charge interaction which goes as \( r^{-1} \)
will be shown to lead to a stable localized excess electron state in
salt melts.

To return to the time-dependent aspects of excess electrons and
their environment, let us consider what happens when the electron is
injected at high energies into the fluid. In radiolysis work the
assumption has been made that the initial state of the electron is
quasi-free (mobile) in that the electron exists in a plane wave state
but the fluid structure is undisturbed and that the trapping or
localization occurs only after the electron has migrated some distance
away from the point of injection, i.e. away from the spurs. Steen,\(^2\)
in trying to fit experimental information into a consistant picture,
has come to the conclusion that this assumption may be erroneous
because in some systems the yield of trapped electrons and the initial
yield of solvated electrons is independent of temperature for the
large variations in the temperatures studied. He interprets this
observation as indicating the recombination prior to trapping is
negligible. Also Steen notes that recombination luminescence studies
indicate that the distribution of electron-cation distances is
independent of whether the ionization is brought about by high energy
radiations or by photoexcitation of levels close to the gas phase
ionization potential.
Figure 1. The optical absorption spectra of trapped electrons in ethanol glass, Curve A was obtained at 4°K after irradiation at 4°K. Curve B was obtained at 77°K after irradiation at 4°K and rapid warming to 77°K. Taken from ref. 3, p. 280.
The point is that this initial (precursor) state is not the same as the quasi-free state nor the same as the localized state and that before either states can occur the initial "hot" electron must become thermalized by a sufficient number of energy losing collisions. Then the important process is competition by a variety of traps for the thermalized electrons. A trap is a potential well in the fluid created by a favorable fluctuation in the fluid (favorable for localization of the excess electron but unfavorable in regard to the total energy of the fluid before the arrival of the electron). When the electron is attracted into a trap, the trap begins to relax as localization proceeds. If relaxation - localization have proceeded to the fullest extent possible the electron is said to be "solvated".

Many experiments have been concerned with demonstrating this relaxation process. The time span for this process begins with the introduction of the electron into the fluid and ends when the fully developed optical absorption band is observed. A fully developed optical absorption band is characteristically broad, lacking in fine structure, and asymmetric to the high energy side. (Figure 1) Kevan has written an extensive review of this area of research and only a cursory overview will be given here.

The simplest way to study the relaxation process is to cool the liquid so as to obtain a glassy matrix. This glassy matrix will then represent a snapshot of a fluid configuration and consist of many traps of varying depth. Thus, when the glass is irradiated, usually at 4°K, the electrons will become trapped in a distribution of potential wells. An example of an optical spectrum obtained in this way is shown in Figure 1, curve A. Although the peak is at 1500 nm
(nanometers), the high energy tail extends beyond 400 nm. indicating that the electrons occupy both shallow and deep traps. As can be seen in Figure 1, curve B, taken after the glass had been warmed to 77°K, the spectrum shifts to the blue. If the warming is done suddenly by plunging the 4°K sample directly into liquid nitrogen, the total integrated absorption decreases only slightly. If the glass is warmed slowly, at a rate of about one degree per minute, nearly half of the trapped electrons are lost by the time 77°K is reached. When this sample is recooled to 4°K, the optical spectrum is essentially unchanged except for a small blue shift which is probably, at least in part, due to the volume contraction of the matrix.

Experimental evidence suggests that at least one bound excited state exists and that the absorption is due, for the most part, to the transition from the ground state to the bound excited state. However, the origin of the width of this absorption and the nature of the excited state is of great interest to the experimentalists as well as the theorists. Of primary interest is the lifetime and the non-radiative decay processes of the excited state.

If only one common characteristic energy is associated with a trap, as in the case for liquids, then the absorption band is said to be "homogeneously broadened" and the band width is a feature of a single trap. On the other hand, if a variety of traps exist with a distribution of energies, as is the case for most glassy matrices, then "heterogeneous broadening" of the absorption band will occur. Bleaching experiments using intense light fluxes to disturb the Boltzmann (normal) distribution in the ground state and in the
excited state can cause a decrease in absorptance. This type of experiment gives us insight into which broadening effect is involved. A uniform bleaching of the absorption implies homogeneous broadening, but the appearance of "holes" in the band imply heterogeneous broadening. Steady-state bleaching experiments which involve long time-exposures to a bleaching light have been done on glasses. Hager and Willard \(^4\) demonstrated non-uniform (selective) bleaching in organic glasses. This supports the idea that the absorption band is due to the excitation of electrons in different potential wells (traps) in glasses.

On the other hand, there is no evidence for a distribution of trapping sites in liquids. Photobleaching of the relaxed state of the extra electron in water (the hydrated electron) and especially in ammonia and amines has been studied by several research groups. Time-resolved bleaching has been used and estimates of the lifetime of the excited state can be made. Kenney-Wallace and Walker \(^5\) observed no bleaching and estimated the lifetime of the hydrated electron to be less than 6 picoseconds in ammonia. Huppert, Struve, Rentzepis and Jortner \(^6\) observed uniform bleaching with recovery occurring within the smallest time-resolution of their apparatus (3.3 pico-seconds). They estimated the relaxation time of the excited state to be around 0.2 picoseconds. Since fluorescence has not been observed in these systems, some non-radiative mechanism must be responsible for repopulation of the ground state. Huppert et al. \(^6\) infer that the non-radiative relaxation to the ground state proceeds without involvement of thermal ionization to an intermediate quasi-free state and they seem to favor a mechanism proposed by Kestner and
Jortner\textsuperscript{7} in which the nuclear configuration in the excited state relaxes to some other configuration which in turn crosses to the ground state. This corresponds to multiphonon non-radiative relaxation of the trap and can be quite rapid.
B. STABILITY CRITERIA

The excess electron in a fluid is found in two essentially different states:

1) The quasi-free state is the electronic function before the fluid is distorted due to its presence. The energy in this state includes the kinetic energy due to scattering from the centers in the fluid and the energy due to electronic polarization interactions. The wavefunction for an electron in a quasi-free state is roughly a planewave

\[ \phi = \Omega^{-\frac{1}{2}} \exp(ik \cdot r), \quad (3) \]

where \( \Omega \) is the volume, \( k \) is the wave vector, and \( r \) is the position vector of the electron. Experimentally this state is usually characterized by high electron mobilities \((100 \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1})\).

2) The localized state is the electronic function when a local fluctuation in the fluid leads to a local permanent distortion. Any further description of this local distortion depends on the nature of the fluid and on the model used to describe the distortion. Regardless of the model, the wavefunction of the excess electron tends to zero for large distances from the localization center. A simple one-parameter wavefunction of the form

\[ \psi_{ls} = (\xi^3/\pi)^{\frac{1}{2}} \exp(-\xi r), \quad (4) \]

or its related guassian form, is usually used for the ground state.
Experimentally this state is characterized by low electron mobilities (less than 1 cm\(^2\) V\(^{-1}\) S\(^{-1}\)).

In polar liquids, polar glasses and in ionic liquids the existence of the localized state can also be confirmed by observing the characteristic optical absorption spectrum. The position of the absorption maximum has been observed to vary from the visible to the infrared depending on the specific medium.

The stability criteria\(^8,9\) for excess electron localization in fluids can be summarized as follows: The total energy of the localized state, \(E_t\), is the sum of two terms. One term is the electronic energy contribution, \(E_{el}\), and the other is the energy required to reorganize the medium, \(E_m\), so that

\[
E_t = E_{el} + E_m.
\]  

(5)

Since the quasi-free state does not distort the fluid \(E_m = 0\).

When the excess electron becomes attracted to a trapping site in the fluid the localized state can become the most favored state energetically and some distortion occurs; in general \(E_m > 0\).

The local distortion can be characterized by a set of configurational coordinates, \(X\), and the most stable configuration is the one for which \(E_t\) is a minimum, i.e.,

\[
\frac{\partial E_t}{\partial X} = 0 \text{ at } X = X_0
\]

(6)

The electron will be localized only if
$E_t(X_0) < V_o$  \hspace{1cm} (7)

where $V_o$ is the ground state energy of the quasi-free electron, i.e. $E_t$ when $E_m = 0$. The important point is that the total energy determines the state of the electron and not just the electronic energy. Also it is important to note that the sign of $V_o$ is not sufficient to determine stability. As can be seen from equation 7, $V_o$ can be negative and the localized state can be the most stable state.

Furthermore the stability criteria discussed above does not predict the absolute stability of the system. What it does predict is the most stable state of the excess electron in a fluid. Since free energy is the true stability criteria, close quantative agreement of $E_t$ with either the Gibbs free energy, $G$, or the Helmholtz free energy, $A$, must be discovered, or alternatively entropy effects must be negligible. This use of energy versus free energy is least serious in the liquid rare gases because the intermolecular forces involved in the formation of the localized state can be accounted for in rather simplistic idea of an electron in a bubble in the fluid. In fact, the purpose of the paper by Hiroike, et al. \(^{10}\) on electrons in liquid helium is to show that the conclusions drawn about these systems are reliable and not artifacts due to the simplifications. It also is the only complete quantum statistical study ever made of such a system. Also in these systems the temperature is generally very low and any entropy effects are expected to be small. Thus free energy changes are very similar to energy changes.
As the temperature increases to room temperature and beyond the entropy contributions become increasingly important. When excess electrons are introduced into polar liquids, Jortner has shown that to a reasonably good approximation the heat of solution of the electron, $\Delta H_e$ is given by

$$\Delta H_e = -E_t(1s) \text{ at } X = X_0$$

(8)

Nowhere in Jortner's development of equation 8 is consideration given to the fact that some hydrogen bonds are broken in the molecules forming the first coordination layer around the localized excess electron.

In one attempt to further understand the relationship between $E_t$ calculated via a model and the free energy, Logan studied the localized state of the excess electron in ammonia-water mixtures. In this model $-E_t(1s)$ is identified with $\Delta H_e$ as Jortner suggests, then an attempt is made to account for the energy contributions that equation 8 neglects. First there is a entropy term which is due to demixing $\Delta S_d$, i.e. the entropy associated with removing a molecule from a bulk fluid and placing it on the first coordination layer of the electron. There is another entropy term, namely the entropy of solvation of the excess electrons in the mixture $\Delta S_s$. Lepourte and Demortier have evaluated the absolute entropies for the ammoniated electron and the hydrated electron. Logan takes the entropy of solvation of the electron to be the sum of the fractions of the number of water or ammonia molecules on the first layer multiplied by the Lepourte and Demortier values for the pure liquids. There is
Figure 2. Ammonia-water mixed solvents: Band maximum versus water mole fraction. The circled points refer to calculations on various cavities - the highest energy point refers to an \((H_2O)_4\) cavity, the next to \((H_2O)_3\) \(NH_3\), etc. The dashed lines connect points based on the lowest free energy differences: \(\Delta G_1\) or \(\Delta G_2\). The solid line is the experimental work of Dye, DeBacker and Dorfman. (Ref. 17) The circled points are from Ref. 12.
Transition Energy, $\hbar \nu$ (eV)

Mole fraction water

$\Delta G_1$

$\Delta G_2$
a third free energy contribution that is considered. It arises from whatever breaking of hydrogen bonds occurs in the formation of the first solvation layer, $\Delta H_{HB}$. According to Logan's model, the solvent molecules of the first layer are assumed not to be bonded to each other as in the bulk fluid. To estimate the magnitude of energies involved, the results of Kollman and Allen were used for the ammonia-water hydrogen bond energies. The results of Baird were used for ammonia-ammonia hydrogen bonds and the water-water hydrogen bond energies of Clementi et al. were used. Realizing that caution must be used in extrapolating these results to the liquid state where the interactions are not expected to be pairwise additive, Logan formulates a method of evaluating $\Delta H_{HB}$. In Figure 2 the calculated transition energy for the most stable state is plotted versus mole fraction water using $\Delta G_1$ and $\Delta G_2$ (dotted lines) as criteria for the most stable "species" where

$$\Delta G_1 = \Delta H_e - T\Delta S_D - T\Delta S_S$$

and

$$\Delta G_2 = \Delta G_1 + \Delta H_{HB}.$$  

(9)

(10)

Each transition energy at one mole fraction is weighted according to $\exp (-\Delta G_1/kT)$ for each species i.e.
\[ \text{hv} = \sum_{N_{\text{H}_2\text{O}} = 0} (\text{hv})_N \cdot \exp \left( - \frac{G_i}{kT} \right). \] (11)

In Figure 2 each circled dot above a mole fraction represents the hv for which the number of molecules on the first solvation layer is four. In each case the lowest transition energy was for the ammoniated electron and the transition energy increases as an ammonia molecule is replaced by a water molecule on the first layer.

The solid line is the experimental work of Dye, DeBacker and Dorfman. The experimental results lie between the theoretical estimates. The energy differences between the clusters is small which seems to indicate that for any given mole fraction there is a distribution of localized sites. In such a case one would expect the half-width of the absorption band to increase considerably for mixtures. This is not observed and Logan concludes that there are features of the mixed solvent calculation that are not well described by the model.
C. NONPOLAR FLUIDS

As a first application of the stability criteria, let us consider the work done on the systems shown in Table 1. The electrons of the molecules of the liquid systems shown in Table 1 may be separated into groups for the purpose of discussion. The first group consists of inner tightly bound electrons of an atomic center. The second consists of valance electrons which are relatively loosely bound. The property of the medium electrons that this separation points out is their polarizability. The valence electrons are those most affected by the presence of an additional electron in the medium.

From studies on the scattering of electrons from these molecules we can separate out the relative importance of the two forces acting between an atom and an electron.

In the lighter systems where all the electrons are rather tightly bound the contribution to the total interaction between atom and electron from the short-range repulsions, which arise from exclusion-orthogonality considerations, overwhelms the longer-range attractions, which arise from polarization of the electron distribution. This leads to an energetically stable localized state for the excess electrons because the electron "pushes" the medium away from its vicinity. A stable configuration is achieved by a balance between the net electron-atom repulsions, the increased kinetic energy of the electron, the contractible force on the void due to surface tension (or its microscopic equivalent) and the pressure-volume work spent in formation of the "bubble". 18
Table 1. Electron Mobility and the Ground State Energy of the Quasi-free Electron in Nonpolar Fluids.

<table>
<thead>
<tr>
<th>Temp $^a$ $^o$K</th>
<th>Mobility $^c$ cm$^2$V$^{-1}$s$^{-1}$</th>
<th>$V_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory $^b$</td>
<td>Exp $^a$</td>
</tr>
<tr>
<td>$^3$He</td>
<td>2.25</td>
<td>4.06x10$^{-2}$</td>
</tr>
<tr>
<td>$^4$He</td>
<td>4.20</td>
<td>2.16x10$^{-2}$</td>
</tr>
<tr>
<td>Ne</td>
<td>22.0</td>
<td>1.6x10$^{-3}$</td>
</tr>
<tr>
<td>Ar</td>
<td>82.0</td>
<td>475,440</td>
</tr>
<tr>
<td>Kr</td>
<td>117</td>
<td>1800</td>
</tr>
<tr>
<td>Xe</td>
<td>163</td>
<td>2200</td>
</tr>
<tr>
<td>H$_2$</td>
<td>20</td>
<td>5.0x10$^{-3}$</td>
</tr>
</tbody>
</table>

$^a$ Taken from Ref. 35.

$^b$ Taken from Ref. 8.
According to the criteria the energetically favorable state in $^4\text{He}$, $^3\text{He}$, $^2\text{H}$, and $^2\text{Ne}$ is a localized state. Experimental confirmation is assured for all of these systems when confirmation is based on electron mobility data alone. In the $^2\text{H}$ system there is a troublesome point in regard to $V_q$. The calculated value $^8$ of $V_q$ is consistent with the criteria, but the experimental value of $V_q$ $^{19}$ does not agree in sign and seems to energetically favor a stable quasi-free state. To resolve this apparent conflict both the theoretical treatment and the experimental work require further analysis.

In helium the localized state is certainly the most stable state both from the theoretical viewpoint $^{20,21}$ and from the experimental viewpoint. $^{22-24}$ The localized excess electron in liquid helium is found to be in a bubble in the helium with a radius of around 11 Å for a pressure of 20 atm. and increases in size with a decrease in pressure. The bubble should be characterized by a relatively high compressibility. This fact has been confirmed theoretically $^{20,25}$ and experimentally. $^{26-29}$ Furthermore, there are theoretical results $^{30}$ that predict a localized to quasi-free transition can occur at sufficiently high pressures because the quasi-free state becomes energetically favorable at these high pressures. The pressure would be so high that the liquid helium would solidify but the bubble would still exist and the transition should occur. Experimental pressures up to 6660 atm. $^{31}$ have been used to look for such a transition but it was not observed. Nevertheless the theoretical results are uncertain enough that the transition could still occur but at even higher pressures.

Studies at low pressures have been done on the helium system and
they agree more closely with theoretical results. If the density of
the system in which an electron bubble has formed is decreased, the
energy of the localized state decreases faster than the energy of the
quasi-free state and a localized to quasi-free transition should be
observed. Since experimentally a system in which the He density in­
creases is easier to construct the system has been studied from low
densities to higher densities. When Levine and Sanders\textsuperscript{32} measured
the electron mobility in liquid helium they observed a dramatic de­
crease in mobility with increasing density. There is no doubt\textsuperscript{20} that
this change in mobility is due to the quasi-free to localized state
transition.

The environment of the extra electron in the liquid Ne represents
the case where the localized state is on the verge of energetic in­
stability. B. Raz and J. Jortner\textsuperscript{33} have predicted that the localized
state will be the most stable one and the low mobility\textsuperscript{34} for this sys­
tem supports this prediction.

No localized state is predicted by stability criteria for Ar, Kr, Xe. In these systems the attractive contribution from the polariza­
tion overcomes the repulsive part of the pseudopotential. The measured
electron mobilities of the systems support these predictions.

Reliable experimental work on electron mobility in nonpolar hy­
drocarbons had to await the development of techniques to highly purify
the hydrocarbons. From 1968 on, measurements in highly purified non­
polar hydrocarbons has been an area of burgeoning interest. Most
measurements have been carried out either by the time-of-flight method
or by observing the increase in conductance produced by a known con­
centration of charge carriers. Many methods for the injection of
excess electrons into the liquid have been used. H. T. Davis et al. have noted two important features of the behavior of electrons in the hydrocarbons studied. First, the electron mobility depends strongly on the structure of the hydrocarbon molecule. For example, at 300°K the electron mobility in saturated n-pentane liquid is about $0.07 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ whereas in neopentane it is about $70 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, which leads them to conclude that as a molecule becomes geometrically more compact and symmetrical the mobility increases rapidly. Secondly, they note that the electron drift velocity, $V_d$, remains linear (i.e., the mobility remains field independent) up to fields much higher than those at which $V_d$ in the liquid rare gases becomes nonlinear. $V_d$ can be calculated from the time-of-flight measurements very easily. Such an experiment measures the drift time, $\tau$, of the movement of a spatial discontinuity of the charge carrier density a known distance, $d$, in an electric field $E$, i.e.,

$$V_d = d/\tau,$$ (12)

The electron mobility, $\mu$, is the proportionality constant between $V_d$ and $E$, i.e.,

$$V_d = \mu E .$$ (13)

Davis et al. have been able to correlate the temperature dependence of $\mu$ in low mobility hydrocarbons quite well with an Arrhenius law, i.e.,
\[ \mu = \mu_0 \cdot \exp(-E_a/kT) . \]  

(14)

Such a temperature dependence for the straight chain, or more generally those hydrocarbons lacking high symmetry, requires that an activation energy, \( E_a \), be overcome before the electrons become mobile and this is consistent with the idea that low mobility electrons are in some sort of localized state. The localized state involved here is rather different than the electron bubble state in the liquid rare gases. Minday, Schmidt, Davis\(^{38}\) conclude that, in the hydrocarbons studied, the dipole moment due to the C-H bonds, which largely cancel out for most molecular conformations when the whole molecule is considered, can offer a dipole field large enough to trap an electron for certain relative orientations. Since the electron is moving between potential trapping sites with thermal speed, it cannot create the trapping configurations but must depend on thermal fluctuations to create them. Once trapped the field of the electron can help stabilize the configuration. With this in mind Kestner and Jortner\(^{39}\) have utilized the effective medium theory\(^{40}\) and four parameters, which were evaluated by fitting the experimental data from Table 2 in the appropriate mobility ranges, to correlate the mobilities with \( V_0 \). The agreement with experimental values of \( \mu \) and \( V_0 \) is encouraging as shown in Figure 3. The authors hope that this will encourage further work in this field.
Table 2. Experimental Data on Electrons in Some Liquid Hydrocarbons.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>T</th>
<th>$\mu$</th>
<th>$V_o$</th>
<th>$\mu_o$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethyilsilane</td>
<td>296</td>
<td>90</td>
<td>-0.61, -0.62, -0.55</td>
<td>194</td>
<td>0.412</td>
</tr>
<tr>
<td>Neopentane</td>
<td>296, 295</td>
<td>67, 70</td>
<td>-0.43, -0.35</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>296</td>
<td>10.9</td>
<td>-0.24, -0.15</td>
<td>84.1</td>
<td>1.2</td>
</tr>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>296</td>
<td>7</td>
<td>-0.15, -0.18, -0.14</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>296</td>
<td>1.1</td>
<td>-0.18, -0.28, -0.17</td>
<td>----</td>
<td>3.5</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>300</td>
<td>0.075</td>
<td>+0.02, -0.01, -0.04</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>296</td>
<td>0.09</td>
<td>+0.09, +0.04, -0.16</td>
<td>67</td>
<td>4.06</td>
</tr>
<tr>
<td>Benzene</td>
<td>300</td>
<td>0.6</td>
<td>-0.14</td>
<td>30190</td>
<td>7.25</td>
</tr>
<tr>
<td>Toluene</td>
<td>298</td>
<td>0.54</td>
<td>-0.22</td>
<td>10.17</td>
<td>2.95</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Ref. 41 for original references.
Figure 3. Electron mobility in liquid hydrocarbons as a function of $V_o$. Dashed line -- Theoretical curve with $E_t = -0.27$ ev, $\xi = 0.255$ ev, $\mu_o = 100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and $x = 6 \times 10^{-4}$. The experimental points for saturated hydrocarbons are: (1) tetramethylsilane, (2) neopentane, (3) 2,2,-dimethylbutane, (4) 2,2,4-trimethylpentane, (5) cyclopentane, (6) n-pentane, and (7) n-hexane. Two aromatic hydrocarbons have been included: (8) benzene and (9) toluene, where negative ion states could contribute to the mobility.

(References to the original data are given in Table 2.)
\[ \mu \text{cm}^2 \text{Volt}^{-1} \text{sec}^{-1} \]

\[ V_0 \text{ (eV)} \]

--- EMT
\[ \xi = 0.26 \text{ eV} \]
\[ E_f = -0.27 \text{ eV} \]
D. POLAR FLUIDS

Some of the work that has been done in polar fluids has already been mentioned in illustrating the time-dependent aspects of the solvated electron and in pointing out the thermodynamic considerations involved in its formation. The purpose of this section is to review the work in polar fluids as yet overlooked.

Research on excess electrons in polar liquids has a longer history than it does in any other media. The discovery of the solubility of the alkali metals in liquid ammonia by W. Weyl over a hundred years ago marks the beginning of the work in polar liquids. Speculation on the nature of the high mobility species in these solutions grew out of the conductance work of Cady and Kraus. Kraus reported a mobility of \(1.08 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) for the negative charge carrier in these solutions, and this is interpreted as supporting evidence for the existence of an electron "species" in metal-ammonia solutions. Further supporting evidence of the localized electron state in dilute solutions of the alkali metals and the alkali-earth metals is the existence of the characteristic asymmetric absorption band. Its peak is found in the infrared in the vicinity of 7,000 cm\(^{-1}\) and is reported to be independent of the solute. This asymmetry of the band extends into the visible region of the spectra and is responsible for the intriguing blue color of the solutions. Other supporting evidence for the localized electron state in the dilute solutions is a single narrow electron spin-resonance line which yields a spin g-factor of 2.0012, very close to the free spin value. This spin-resonance line has been shown to be independent of the solute. In the absence of impurities, the
ammoniated electron has a relatively long life even at room temperature. The rate of decomposition of highly purified sodium-ammonia solutions is less than 1% per day. The ammoniated electron is the primary reducing species in the class of organic synthesis reactions known as Birch reductions.

Speculation on the existence of the hydrated electron has been in the literature since at least 1947. The idea of Lea's was that an electron could have an existence separate from its irradiated parent water molecule. Serious speculation on the independent existence of the hydrated electron came when Stein drew attention to the fact that an injected electron is thermalized in a time on the order of $10^{-14} - 10^{-13}$ s and concurrently undergoes a process of hydration in which it polarizes the medium by digging a potential well. At nearly the same time Platzman, applying the theory of Frank, brought the idea of a hydrated electron into focus. Beginning in 1958 with the work of Hayan and Weiss, Baxendale and Hughes, and Barr and Allen, supporting experimental evidence for the hydrated electron accumulated. In 1962 Hart and Boag made a dramatic observation. They were the first to observe the characteristic spectrum of the hydrated electron and coupled with the additional chemical evidence any disbelief in its existence was stilled. The mobility of the hydrated electron was measured in 1966 by Schmidt and Buck who reported it as $1.84 \times 10^{-3} \pm 2 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$. The electron paramagnetic resonance studies of Avery et al., two years later reported a spin g-factor of $2.000 \pm 0.0002$ for the hydrated electron, which is also very close to the free spin value.

The detection of the hydrated electron is more difficult than
the ammoniated electron due to its much shorter lifetime. In water in which careful attention has been paid to the removal of scavenging impurities and in which adjustment of the pH is made to suppress the fastest reactions, half-lives greater than 0.5 msec have been observed. \textsuperscript{64} Earlier efforts of Linschitz \textsuperscript{65} in 1953 to detect the hydrated electron failed because the sensitivity of detection was too low and not because the time resolution (10\textsuperscript{-5}s) was insufficiently short, as was thought at the time. The short lifetime is a result of the many possible reactions with the many radiation products that are produced along with it. Matheson and Dorfman \textsuperscript{64} discuss six other radiation products that are produced concurrently and the hydrated electron is known to react with four of these.

The first part of this section has dealt with the history of the experimental proof of the existence of the ammoniated electron and the hydrated electron. Once their existence was well established, many experimenters, taking advantage of the tremendous advances in technology within the last ten or so years, began very sophisticated experiments designed to provide new evidence concerning the structure and properties of the solvated electron in other polar media and their mixtures. Mode-locked lasers generating picosecond pulses permit experiments to be done on a time scale where the relaxation of a quasi-free electron to the localized electron state can be observed in water. \textsuperscript{66}

The development of fast infrared detectors allows the observation of the absorption spectra well into the infrared. This detector makes possible the observation of the absorption spectrum of the solvated
electron in a series of weakly polar liquids. In addition, absorption spectra have been observed in a variety of binary liquid systems consisting of two different strongly polar compounds, or a strongly polar and a weakly polar compound, or a strongly polar and a nonpolar compound.

The recent efforts of Dorfman and co-workers\textsuperscript{17,67,68} reveal some puzzling aspects of binary liquid mixtures. The dependence of absorption maximum (\(E_{\text{max}}\)) with mole fraction in the ammonia-water mixtures has already been discussed in the section on stability. The dependence of \(E_{\text{max}}\) with composition in ethylenediamine (EDA)-water mixtures is similar to the ammonia-water dependence of \(E_{\text{max}}\). This dependence in some alcohol-water mixtures is not far from linear; however, in other mixtures \(E_{\text{max}}\) is dominated by water.\textsuperscript{69} Domination by one of the components even though a large percentage of the other component is present occurs in other mixtures as well. For example, in EDA-Ethanol mixtures, \(E_{\text{max}}\) is dominated by EDA; in water-ether mixtures, water dominates, but in EDA-ether the dependence is very nearly linear. As yet no obvious pattern has developed but one point is clear: any description of solvated electron systems must rely on more than the bulk properties of the solvent.

Another area where some of the more subtle and hence interesting properties of the solvated electron are revealed is in the work on dense polar vapors. Olinger et al.\textsuperscript{70} report the density dependence of \(E_{\text{max}}\) in supercritical ammonia. They were able to repeatedly change the density between 0.6 and 0.05 \(\text{g/cm}^3\) by varying the pressure between 1.00 and 100 atm. at a temperature of 150°C. The shape of the spectrum and the position of \(\lambda_{\text{max}}\) are only slightly changed from normal liquid
ammonia at 25°C indicating that solvation is possible even at low densities. A plot of optical density divided by mass density versus mass density, i.e. yield per gram versus density, remains more or less constant down to a density of 0.2 g/cm$^3$; below which the yield per gram drops sharply. The behavior of $E_{\text{max}}$ with density is interpreted by the model of Copeland et al.\textsuperscript{71} In this model the polaron coupling parameter $\beta = D_{\text{op}}^{-1} - D_{\text{s}}^{-1}$ is expressed in terms of the optical dielectric constant $D_{\text{op}}$ (computed as a function of density by the Clausius-Mossoti relation) and the static dielectric constant (computed as a function of density by the Onsager relation). The quasi-free energy of the electron, $V_Q$, was computed via the same model. The remarkable feature of these results is that a plot of $\beta$ versus density is almost constant down to 0.16 g/cm$^3$ and then drops rather steeply, while a plot of $V_Q$ versus density is small and negative changing gradually over this density range. Olinger et al. conclude that the model provides an adequate interpretation of the observed behavior.

In a later paper Olinger, Bahne and Schindewolf\textsuperscript{72} repeated the experiment using deuterioammonia in order to remove the strong interference of the vibrational absorption spectrum of ammonia with the absorption spectrum of the ammoniated electron. The deuterioammoniated electron absorption spectrum has about the same form and the same position as it has in normal liquid ammonia. The same behavior of $E_{\text{max}}$ with density was observed. When the companion electron mobility studies in the relevant density ranges are done we will know whether or not the localized to quasi-free transition of the excess electron in ammonia has been observed.
Gaathon et al.,\textsuperscript{73,74} on the other hand, were unable to reach densities low enough along the liquid-vapor curve in D\textsubscript{2}O to observe the dramatic drop in yield that was observed in NH\textsubscript{3} and in ND\textsubscript{3}; they observed the hydrated electron spectrum down to densities as low as 0.02 g/cm\textsuperscript{3}. Michael et al.,\textsuperscript{75} while they did not set out to find the minimum density that would support a hydrated electron, have observed its spectrum in supercritical D\textsubscript{2}O to densities as low as 0.2 g/cm\textsuperscript{3}.

Newton\textsuperscript{76,77} in his ab initio level calculations on water and ammonia found that at the minimum in the absolute energy of (H\textsubscript{2}O\textsubscript{4}), the difference between the tetrahedral arrangement of dipole-oriented water molecules and the same arrangement plus an extra electron at the center is around -0.16 ev. A well of this magnitude will not lead to room temperature stability if thermal population of intermolecular vibrational modes and entropy effects are also considered. However, when Newton included the long range contribution of the continuum in liquid water at room temperature this energy difference is -1.62 ev.

When Newton's results are considered together with the density experiments, Newton\textsuperscript{77} concludes that more than four water or ammonia molecules are needed for electron trapping under equilibrium conditions at room temperature or above.

Although studies on the emission of electrons from the surface of only two solvents - liquid ammonia and hexamethyl phosphoric triamide (HMPA) which is also known to contain solvated electrons have been done - Delahay and co-workers\textsuperscript{78-80} believe that the phenomenon of photoelectron emission (PEE) from solutions is a general phenomenon for solvated electrons. Irradiation by light with a wavelength less than
1000 mm of the surface of the liquids causes emission of electrons into the solvent vapor above the solution. This emission can be detected by means of an apparatus resembling, at least in principle, a vacuum photodiode. A cup containing the emitting solvated electron solution faces a collector electrode located in the gas phase. The diode circuit is completed by a current detector and power supply. Two types of information can be obtained: 1) The spectral response for emission yield, i.e. a plot of the number of emitted electrons per incident photon versus photon energy is obtained, and 2) The number distribution of emitted electrons as a function of their kinetic energy for monochromatic irradiation is obtained. The plot obtained in (2) is an energy distribution curve (EDC) at a given photon energy. Delahay's research group has developed a method for determining the functional dependence of the photoionization cross-section on photon energy from energy distribution curves. Furthermore, the spectral response curves in conjunction with the absorption spectra provide criteria for establishing the occurrence of photoionization via autoionization of bound excited states. The evidence for autoionization of anthracene ions is conclusive; however, the evidence for autoionization in the liquid ammonia and HMPA is less convincing. This point must be clarified before the mechanism for bound-continuum transitions (i.e. transitions from the localized state to the quasi-free) can be unequivocally established in these systems. Their hope is to find the energy of the onset of the bound-continuum transitions for the solvated electrons in liquids. Problems arise because the PEE spectrum of the ammoniated electron exhibits two bands. At present
Delahay suggests that the first band with its high energy tail is due to bound-continuum transitions, while the second band at higher energy and symmetric in appearance is due to bound-bound transitions with autoionization of the bound excited state.

An interesting extension of the work on photoionization cross-sections suggested by Delahay\(^{80}\) is that the potential in which the solvated electron exists might be calculated using the graph of cross-section versus photon energy. A fledgling calculation of this nature has been reported.\(^{81}\) However, it is plagued by the same problems as are all attempts to obtain a potential from limited knowledge of some of the integrals containing it, i.e. the problems of transforms based on limited data.
E. IONIC FLUIDS

The purpose of this section is to review the previous work done on molten salts and to discuss the ideas that have developed from this work, so as to provide a background for the model of a trapped excess electron developed in Chapter II.

Binary metal-molten salt solutions are often divided into two categories for discussion. The division is based on the increase in specific conductance when small amounts of the metal are added to the corresponding molten salt. Type one solutions are those that show large increases in the specific conductance when small amounts of the metal are added. Type two solutions are those that show small increases in the specific conductance when small amounts of the metal are added. The type one solutions have relatively simple phase diagrams. They show no evidence of new compound formation and the one feature that sets their phase diagrams apart from the simplest monotectic ones is an area where two immiscible liquids form. Type two solutions have far more complicated phase diagrams than type one solutions indicating the formation of new compounds in the melts. For example, in Bi-BiCl₃ solutions, Hershaft and Corbett have identified the polymeric species Bi₁₂Cl₁₄.

Generally type one solutions are intensely colored, and the high specific conductance is assumed to be mostly electronic in nature. On the other hand, type two solutions have a metallic luster, and the specific conductance is assumed to be mostly ionic in nature. An example of a type one solution is K-KCl.
When 0.1 mole fraction K is added to molten KCl at 82°C, which is above the consolute temperature of 79°C which occurs at about 0.4 mole fraction K, the specific conductance increases from 2.3 ohm\(^{-1}\) cm\(^{-1}\) for the pure molten salt to 32.0 ohm\(^{-1}\) cm\(^{-1}\). Similar behavior is observed for the other K - KX systems, where X = F, BR, I.

An example of a type two solution is Bi - BiCl\(_3\). When 0.09 mole fraction Bi is added to molten BiCl\(_3\) at 575°C, which is not above the consolute temperature of 780°C, which occurs at about 0.5 mole fraction Bi the specific conductance only increases from 0.49 ohm\(^{-1}\) cm\(^{-1}\). This is the highest temperature at which the specific conductance was measured in the single liquid phase above 250°C from 0.0 mole fraction Bi to at least 0.3 mole fraction. Similar behavior is observed for the other Bi-BiX\(_3\) solutions, X = Br, I.

The solutions Na-NaX (X = Cl, Br, I) are type one solutions with phase diagrams similar to the K-KX systems, however the shape of the specific conductance versus mole fraction metal curve at low concentrations is quite different. Both curves increase with increasing mole fraction metal but the K-KX system curves are concave upward whereas the Na-NaX system curves are concave downward. All of the Na-NaX experiments were done below the consolute temperature and only in the Na-NaI system can the inflection point be observed. It occurs around 0.06 mole fraction metal with a specific conductance of 8.0 ohm\(^{-1}\) cm\(^{-1}\) at 900°C.
The explanation advanced by Bronstein and Bredig\textsuperscript{85,90} for this decrease in conductivity in the Na-NaX systems is that the electrons are trapped in the lower energy state of the covalent bonds of the diatomic metal molecules, which inhibits their participation in the conduction process. The occurrence of similar behavior in Na-NaCl and Na-NaBr systems in combination with the observed positive deviation from Raoult's law\textsuperscript{99} is interpreted in terms of the formation of diatomic molecules Na\textsubscript{2}.

Bronstein and Bredig are able to more dramatically depict this difference in behavior by defining a characteristic or apparent equivalent conductance of the dissolved metal $A_m$ by the equation

$$A_m = (A_{\text{soln}} - (1 - N_m)A_{\text{salt}})/N_m,$$  \hspace{1cm} (14)

where $A_{\text{soln}}$ and $A_{\text{salt}}$ are the equivalent conductances of the solution and the pure salt. $N_m$ is the equivalent fraction of the metal. $A_m$ represents the change of the conductance caused by the addition of one equivalent of metal to an amount of salt contained in the solution of given composition which is between two electrodes 1 cm apart. When a plot of $A_m$ versus mole fraction metal is made the conductance in the K-KX systems rises monotonically with an increasing rate with increasing mole fraction metal; in the Na-NaX systems $A_m$ drops rapidly toward a minimum which would be followed by a rise if the phase boundary line for two immiscible liquids were at larger metal concentrations for the Na-NaCl and Na-NaBr systems. The minimum can be observed in the Na-NaI system. In this system the plot of $A_m$ versus mole fraction metal
drops sharply from $12,000 \text{ ohm}^{-1} \text{ cm}^{2} \text{ equiv}^{-1}$ to a minimum of $4,800 \text{ ohm}^{-1} \text{ cm}^{2} \text{ equiv}^{-1}$ at 0.075 mole fraction metal at 900°C.

In summary, the evidence considered above suggests that the distinction between the two types of solutions depends on the kind of trap that exists for the valence electron of the added metal atom. On the one hand, there is a trap which is deep and is essentially chemical bonding in nature. This is the nature of the trap found in Bi-BiCl$_3$ system which yields the Bi$_{12}$Cl$_{14}$ or possibly in the Na-NaX systems which yield Na$_2$ on the addition of the metal. In the other Bi-BiX solutions there is no significant electronic contribution because the oxidation state of the Bi can decrease. In general then, type two solutions exhibit ionic conductivities because charge transfer from the excess metal atom to some molecular complex or another metal ion is virtually complete. On the other hand those solutions which show strong electronic contributions to their conductivity have shallow traps. The nature of these electron traps is the subject of much speculation, and a definitive theory accounting for all the known facts (spectroscopic, magnetic, thermodynamic, and transport properties) has yet to be put forward. The state of the electron involved in the high conductivity melts is our primary interest. Further considerations will be limited to the first type of systems and to that area of phase diagram where there is a single liquid phase, or to the pure molten salt. We will refer to the trapped electron by the general term "solvated electron."

Spectroscopic studies of excess electrons in molten salts were a natural continuation of the first study of F-centers at
Gottingen by Hilsch and Pohl. Following their work Mollwo investigated the temperature dependence of the band maxima and the full width at half maximum absorption (FWHM) of F-centers in nine alkali halides. He observed a quadratic relation between the wavelength of the absorption maximum $\lambda_{\text{max}}$ and the lattice parameter $d$, i.e.

$$\lambda_{\text{max}} = A d^2,$$  \hspace{1cm} (15)

where $A$ is the proportionality constant determined by fitting the equation to the data. He also observed that as the temperature is increased $\lambda_{\text{max}}$ shifts to longer wavelengths, a fact which is consistent with an expanding lattice if equation 15 is assumed.

In 1935 Mollwo extended his work on alkali halide F-centers to temperatures just above their melting points, and observed that $\lambda_{\text{max}}$ is abruptly shifted to longer wavelengths on melting and that the FWHM is greatly broadened compared to the F-center value. In 1969 Gruen and co-workers repeated Mollwo's work using sapphire cells in order to avoid the problems Mollwo encountered due to discoloration of the glass absorption cells. Their data closely agrees with Mollwo's and they reanalyzed his data using accurately measured densities for the molten alkali halides to calculate molar volumes, $V_m$, as a function of temperature. This effect of the large volume expansion on melting was found to fit the same relation that applies to F-centers, namely

$$\lambda_{\text{max}} = A' V_m^{2/3},$$  \hspace{1cm} (16)

using the relation that $d^2$ is proportioned to $V_m^{2/3}$.  

Table 3 is a chronological listing of the researchers who are thought to have observed a solvated electron in salt melts. Only their data on pure molten salts or metal-molten salts mixtures has been listed. For the most part, what has been left out of the table is the work on molten salt-salt mixtures. Three different methods of generating excess electrons have been used. Entries in the "melt" column which appear as metal/salt indicate that the absorption observed is believed to be due to the solvated electron from the dilute solution of the dissolved metal. In this case, the salts are said to be additionally colored. The technique originates with Davy,\textsuperscript{103} who in 1807 discovered that metals dissolve in molten salts. Injection of excess electrons into a salt melt by pulse radiolysis began with Black and Compton.\textsuperscript{98} Unfortunately they did not publish their spectra. Black and Compton concluded that the observed absorption is similar to that produced by the additively colored alkali halides, and they attributed the absorption to solvated electrons. Black and Compton also observed a moderately intense radioluminescence which interfered with the absorption measurements. However, the luminescence could be measured independently by closing a shutter between the lamp and the sample. The absorption signal could then be corrected by subtracting from it the corresponding fluorescence signal. If this fluorescence is really due to the solvated electron, then it is the only such observation. The decay of the optical density shows a long-lived component with a time constant of about seven microseconds.
Table 3.

Observed Absorption Maxima in some Molten Salts.

<table>
<thead>
<tr>
<th>Author Year</th>
<th>Melt</th>
<th>Temp. °C</th>
<th>$E_{\text{max}}$ (ev)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Mollwo 1935</td>
<td>Na/NaCl</td>
<td>*</td>
<td>1.57</td>
<td>93</td>
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<tr>
<td></td>
<td>Na/NaBr</td>
<td>*</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Na/NaI</td>
<td>*</td>
<td>1.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K/KCl</td>
<td>*</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K/KBr</td>
<td>*</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K/KI</td>
<td>*</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>Young 1963</td>
<td>Li/LiCl</td>
<td>650</td>
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<td>95</td>
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<tr>
<td>Greenburg, Warshawsky 1964</td>
<td>M/Li-KCl</td>
<td>400</td>
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<td></td>
<td>M=Li, Na, K</td>
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<tr>
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<td>Na/NaI</td>
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<td>2.17</td>
<td></td>
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<tr>
<td>Black, Compton 1965</td>
<td>KCl</td>
<td>*</td>
<td>1.17</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>KCl-KBr</td>
<td>*</td>
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</tr>
<tr>
<td>Rounsaville, Lasowski 1968</td>
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<td>1.53</td>
<td>99</td>
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<tr>
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<td>K/KCl</td>
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<tr>
<td></td>
<td>K/KBr</td>
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</tr>
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<td></td>
<td>Cs/CsCl</td>
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<td></td>
<td>K/KNH$_2$</td>
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Table 3. Continued

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<thead>
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<th>$E_{max}$(ev)</th>
<th>Ref.</th>
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<td>100, 101</td>
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<td>Zhukova, NaI</td>
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<td>&quot;</td>
<td>800</td>
<td>0.92</td>
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* Near the melting point.
a. Electrons injected by pulse radiolysis.
b. Reported fluorescence from melt.
c. Electrons injected by A-C electrolysis.
Pikaev and co-workers\cite{100,101} also inject excess electrons into salt melts by pulse radiolysis and their spectra have many features similar to the characteristic spectra of solvated electrons in polar liquids. Pikaev et al. report that the lifetime of the absorption in all melts studied is not more than two microseconds, and they believe the absorbing species to be a thermalized electron autolocalized in a "cavity."

The third method that has been used to generate excess electrons in molten salts is periodic injection by AC-electrolysis. This method is employed by Schmitt and Schindewolf\cite{102} who also report that the spectrum of the absorbing species has features similar to the characteristic spectra of solvated electrons in polar liquids.

When questions about the local environment of the absorbing species in molten salts were discussed in the literature two sets of language have been used. The F-center set which undoubtedly originates with Mollwo, and the "cavity" set which has more recent origins.\cite{96,99,104} What, if any, is the difference between the two descriptions? To say that the absorbing species in a molten salt is essentially an F-center implies more than we know. For example, we do not know how many nearest neighbors the extra electron has in a molten salts. X-ray and neutron diffraction data might help answer this question, even though unambiguous resolution of the data is in general difficult, if not impossible. This point will be discussed in more detail later. Nevertheless, the data is interpreted as clearly showing that there are less
than six nearest neighbors to the cavity electron.\textsuperscript{105} Furthermore, to describe the local environment as an F-center also implies that the nearest neighbors are very rigidly positioned which is not the case in molten salts as is indicated by the dramatic change in the FWHM on melting. Also, considering the liquid nature of a molten salt, the number of nearest and next nearest neighbors is unlikely to be constant with time.

The definition of an F-center could be relaxed enough to describe the local environment of the solvated electron in melts, but since it is so different from ordinary F-centers, the cavity description seems more appropriate.

We will assume that the solvated electron in molten salts is localized in a negative ion vacancy in the melt whose nearest neighbors are the metal ions of the melt.

From studies on molten salt mixtures\textsuperscript{101,102} we conclude that if the two metal ions are of nearly equal size in a mixture, then the number of each metal ion on the first coordination layer is determined by the mole fraction metal of the mixture. As the difference between the sizes of the metal ions increases, the number of smaller metal ions on the first coordination layer is larger than the mole fraction of that metal would indicate, i.e. the influence of the smaller size metal prevails.

The next nearest neighbors are the halide ions. Their number and position are essentially determined by the coulombic interactions and statistical mechanics of the melt including the extra electron. Their distribution around the cavity electron
will depend on the characteristics of the cluster containing the metal ions and the electron. The size of this cluster is not determined by the dimensions of the crystal lattice nor by the size of the anion vacancy that may have initially trapped the electron. The number and the position of the ions will be discussed more fully in Chapter II.

When an alkali halide melts, the ions formerly fixed in the rigid lattice become free to move and adopt modified interparticle distances. Experimental observations show that most salts melt with a considerable increase in volume. For the alkali halides, the volume expansion on melting is on the order of 20\%.\textsuperscript{106} Computer simulations of the alkali halide melts give some insight into the movement of the ions on melting.\textsuperscript{105,107-111} The behavior of the peaks in the pair distribution functions (PDF) as the temperature increases through the melting point show little change. The position of the first peak and the height of the first peak in $g_\rightarrow(r)$\textsuperscript{105} are almost constant with the most notable changes occurring when there is a large difference between the cation and the anion size.\textsuperscript{109} More interesting are the changes which occur in $g_\leftrightarrow(r)$ and in $g_\rightarrow(r)$ on melting. The height of these peaks decreases by a factor of nearly two, and they broaden significantly. As an example, for KCl $g_\leftrightarrow(r)$ is like $g_\rightarrow(r)$ because of the similarity in ion sizes, and makes resolution of the like ion PDF, $g_\leftrightarrow$, unnecessary. The height of the first peak in $g_\leftrightarrow(r)$, $h_\leftrightarrow$, in the solid at $1045^\circ$K is 3.12, whereas for the liquid at this temperature it is 1.79. This behavior is consistent with the fact that
on melting an expansion occurs and, more importantly, there is an incipient formation of ion pairs at a separation corresponding closely to the minimum in the effective cation-anion pair potential energy curve.

Many of the computer simulations of molten alkali halides have used the effective pairwise additive potential of Born-Mayer-Huggins$^{112}$ as parameterized by Tosi-Fumi$^{113,114}$ (BMH-TF). The form of the potential in atomic units as used in the computer simulations, as well as in the model calculations of Chapter II, for the metal-metal (+ +), the halogen-halogen (− −), and the metal-halogen (+ −) interactions is,

\[
\psi(r_{ij}) = \frac{Z_i Z_j}{r_{ij}} + A_{ij} \exp(B(\sigma_i + \sigma_j - r_{ij})) + C_{ij}/r_{ij}^6 + D_{ij}/r_{ij}^8 ,
\]

(17)

where i and j can be either + or −. The system is assumed to be fully ionic so that \( Z_+ = +1 \) and \( Z_- = -1 \). The first term is the long-range charge-charge interaction. The second term represents the electron shell repulsion interaction. It also includes the effect of the ion induced dipole interaction which should vary as \( r^{-4} \) and be attractive.$^{105}$ The last two terms are the short-range induced dipole-induced quadrupole attractive dispersion interaction.

In the Tosi-Fumi parameterization, the dispersion constants are not adjustable but fixed according to the spectroscopic determination of Mayer.$^{115}$ For the short-range repulsive term they$^{114}$ make the following assumptions: 1) \( B \) is a constant for a crystal but varies from crystal to crystal, 2) When \( A_{ij} \) is
written in the form

\[ A_{ij} = b \cdot B_{ij} \]  

(18)

the value of \( b \) is constant for all crystals, and for all interaction types. \( \sigma_i \) and \( \sigma_j \) are the ionic radii, which depend only on the ions involved. The Pauling \(^{116}\) factors, \( B_{ij} \) are defined by

\[ B_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \]  

(19)

with \( n_i, n_j \) the number of electrons in the outer shells, usually eight, except for \( \text{Li}^+ \) which has \( n \) equal to two. Therefore for the 17 alkali halide salts, which they considered, the parameters required are 17 values of \( B \), five values of \( \sigma_+ \), four values of \( \sigma_- \) and one value of \( b \). Tosi and Fumi obtained these parameters by a least squares fit to the Hildebrand equation of state and its volume derivative at constant temperature. The experimental data required for each salt are the lattice parameter, the coefficient of volume thermal expansion, the isothermal compressibility and its temperature and pressure derivatives.

The shortcomings of the BMH-TF potential arise because 1) it is a central potential, and 2) it neglects many-body interactions. Because BMH-TF is a central potential, it must satisfy the Cauchy relation for the elastic constants of a crystal, i.e. \( C_{12} = C_{44} \). Experimentally there is often considerable difference between \( C_{12} \) and \( C_{44} \). Many-bodied effects have been neglected, for the most part, in the computer simulation of molten salts, but in view of the excellent results their neglect does not seem serious.
"We should bear in mind that the purpose of theory is not to reproduce experiment but rather to provide a deeper understanding of the real world."

Joshua Jortner
in Electrons in Fluids
A. AN OVERVIEW OF THE MODEL

The main thrust of this research is to develop a model that accurately accounts for the major interactions which lead to a stable localized state of the excess electron in molten alkali halide melts.

Even if one is clever enough to perform accurate calculations on an F-center in a lattice, the difficulties faced when this type of center is introduced into a liquid are even greater. The problem of accurately separating the motion of the extra electron from the motion of the nuclei in the liquid is somewhat more serious than it is in separating the F-electron from the lattice. The qualitative picture of this situation is that the electron "sees" and responds to the instantaneous movement of the melt, but the melt only responds to the average position of the extra electron. Even under the melt temperatures this description should be reasonable and is the basis for making the Born-Oppenheimer approximation.

In regard to optical transitions we further assume that the melt is a ponderous medium that moves very little, in fact not at all, during electronic transitions. This is the Franck-Condon principle and it leads to the so called "vertical" transitions. The melt does provide the potential for the electronic states and the movement of the melt has the effect of changing the potential which the cavity electron sees, and in doing so changes its electronic energy levels. This leads to a broad bandshape and not a single line.
A convenient and useful way of visualizing optical processes of an extra electron in a molten salt is through the use of a configuration coordinate diagram. In reality, the state of this system is given by a set of coordinates, \( q_n \), corresponding to the number of degrees of freedom, \( N \), of the system and the total energy of the system, \( E^T(q_1, \ldots, q_j, \ldots, q_n) \) is some function of these coordinates. Therefore, \( E^T(q_n) \) is a multidimensional surface. Now let us simplify the real situation to the point at which these calculations are done.

We assume that the energy of the system, which is taken to be the extra electron and its first solvation layer, is most sensitive to the radial motion, or "breathing" modes of the ion pairs. The basic assumption is of course, incomplete in that there are other modes of vibration, and the cavity electron may be significantly coupled to more than the first solvation shell (especially in its excited state). Nevertheless, these assumptions allow us to develop a qualitatively useful model.

In our model, two configuration coordinates are used (Figure 4). \( R \) is the distance from the localization (cavity) center to a metal ion, and \( D \) is the distance from a metal ion to the nearest halogen ion, which will be assumed to lie along the radius vector from the center of the cavity to the cation for computational simplicity. The equilibrium ground state energy is given by \( E^T_G(R_G, D_G) \), and the equilibrium excited state energy is given by \( E^T_E(R_E, D_E) \), where \( R_G, D_G \) and \( R_E, D_E \) are the appropriate state equilibrium coordinates. \( R \) is the variational parameter used to minimize the total energy of the system; it is the parameter that characterizes
Figure 4. Definition of the distances involved in the model. $R_H$ is the radius of the anion. $R_M$ is the radius of the cation. $D$ is taken to be the distance to the first peak in the pair distribution function. $R$ is the cavity radius. $R_V$ is the void radius.
the melt's response to the average electron density distribution of the localized electron and is similar in nature to the internuclear distance in a molecular Hartree-Fock calculation. The coordinate D should not be thought of as a variational parameter used to minimize the total energy. In this calculation it is taken equal to the position of the first peak distance in the pair distribution function, $g_{+-}(r)$, when the total ground state or excited state energy is calculated. Its purpose is to characterize the dynamic and long-range coulombic nature of the medium. We shall later see that this provides us a way to introduce the effect of the medium on the asymmetry of the bandshape.

Even after making the Born-Oppenheimer approximation and successfully decoupling the cavity electron from the melt nuclei, thereby reducing the calculation to an electronic one, there are still serious problems in treating the electron-ion interactions. For no matter what model we assume there are many electrons bound to the individual ions on the first solvation layer of the cavity and their effects must be considered.

These effects can be treated exactly within the Hartree-Fock framework if we want to treat all of the electrons. The total wave function of the many-electron system is written as the antisymmetrized product of the spin-orbitals

$$
\phi(0, 1, 2, \cdots n) = A\{\phi_0(0)\phi_1(1) \cdots \phi_n(n)\},
$$

(20)

where $A$ is the usual antisymmetrizing operator and $n$ is the number of electrons. $\phi_0(0)$ denotes the cavity electron. By varying the total energy with respect to the spin-orbitals we obtain a one-
electron eigenvalue equation of the form

\[(T + V)\phi_i = \varepsilon_i \phi_i \quad (21)\]

where \(T\) is the kinetic energy operator and \(V\) is the potential arising from the field of the nuclei and all the other electrons. The spin-orbitals are usually taken as mutually orthogorial, i.e.

\[\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (22)\]

We want, however, to simplify the problem to a one-electron one (the cavity electron) by using an effective one-electron potential that includes two major effects. First, the electron-nuclei terms tend to cancel some of the electron-electron repulsions in \(V\) of equation 21. Second, the total wave function is antisymmetric which means a sort of Pauli exclusion principle applies, i.e. electrons tend to stay out of one another's way.

The idea that the many-electron problem could be reduced to a one-electron problem was introduced by Hellmann and Kassatotschkin\textsuperscript{117,118} (HK), who called it the "combined approximation." HK were interested in calculating the binding energy of the valence electron in metals. This method begins by treating simultaneously the atomic cores according to the Thomas-Fermi model and the valence electron by the more correct Schroedinger equation. The "approximated" Schroedinger equation for the valence electron is obtained from the variation principle for the total energy and is

\[(-\frac{\hbar^2}{2m} + V_{HK}(r)) \psi(r) = \varepsilon \psi(r) \quad (23)\]
$V_{HK}(r)$ is a form of a pseudopotential and $\psi(r)$ is the spatial one-electron wavefunction for the valence electron.

The HK potential for the valence electron contains the familiar electrostatic interaction of the closed shells on the valence electron as well as an additive term of the form $\partial T/\partial \rho$ where $T$ is the kinetic energy per unit volume of the paired electrons and $\rho$ is their density. Thomas-Fermi theory gives,

$$\frac{\partial T}{\partial \rho} = \frac{\hbar^2}{8m} \left( \frac{3\rho}{\pi} \right)^{2/3} . \quad (24)$$

HK take

$$\frac{\partial T}{\partial \rho} = \frac{c}{r} \exp \left( -ar \right) . \quad (25)$$

Thus, the potential $V(r)$ from equation 23 is then of the form

$$V(r) = -\frac{Z}{r} + \frac{c}{r} \exp \left( -ar \right) . \quad (26)$$

The purpose of the repulsive potential is to keep the valence electron from "falling" into the core and is one method of including the short-range Paul exclusion "forces." A one-parameter hydrogen-like wave function is then used in equation 23 and $c$ and $a$ are determined from the two lowest $S$ terms of the metal spectra. Callaway$^{119}$ points out that the wave functions are poor approximations to the true wave functions for the Hellmann potential and consequently may lead to erroneous estimates as to the range and strength of the repulsive term of this form for $V(r)$. The values determined this way by HK for sodium and potassium are given in table 4.
A method for determining the potential parameters for the halogens from those of the metals has been reported by Thommen. This method takes advantage of the closed shell nature of the ions and hence the parameters for the potential can be correlated with their size. The values determined for the halogens by Thommen are given in table 4.

Since Hellmann's introduction of pseudopotentials it has been realized that in an atom, molecule or solid there is almost complete cancellation between the large negative potential, $V$ of equation 21, felt by a valence electron when inside the core of an atom and its large positive kinetic energy which is inherent in the oscillations of its wave function $\phi_v$ there.

This property can be used to reduce the many-electron problem to a one-electron problem by transforming the wave equation for the valence electron

$$(T + V)\phi_v = E\phi_v$$

into

$$(T + V + V_R)\psi_v = E\psi_v ,$$

where $V_R$ is a nonlocal repulsive potential which cancels most of $V$, leaving a weak net potential $(V + V_R)$. This potential is called the pseudopotential, $V_{ps} = V + V_R$, and $\psi$ is the pseudo-wave function which is equal to $\phi_v$ outside the atomic core, but inside the core has the oscillations of $\phi_v$ removed. The problem of determining the energy levels and the wave function reduces to solving the one-electron wave equation.
Kubler and Friauf\textsuperscript{124} (KF) have developed a technique for solving the many-electron problem for the F-center electron based on pseudopotential theory.\textsuperscript{121, 123} KF separate the electron-ion terms out of $V$, neglect exchange terms and then make a "localized approximation" by removing the F-electron wave function, $\psi_F$, from inside certain two-center integrals by assuming that $\psi_F$ is relatively constant in the vicinity of the nearest neighbors.

There are two advantages to this approach. First, the smooth envelope function $\psi_F$ in equation 29 has simple forms for the lower energy states of the excess or F-center electron, and with the nearly spherical symmetry of the cavity or the F-center the first two states are approximately 1S and 2P in character. Second, $\psi_F$, is much easier to obtain from numerical methods than $\psi_F$.

Using the free-ion HF orbitals for Na\textsuperscript{+}, K\textsuperscript{+} and Cl\textsuperscript{−}, KF numerically evaluated the appropriate pseudopotentials. The resulting potentials for each ion are then fitted by a small number of simple exponentials of the same form used by HK namely,

$$V_{KF}(r) = \sum_{n=1}^{N} (c_n/r) \exp(-\alpha_n r).$$

The values determined by KF in this way are given in Table 4.

In summary, in our model we shall assume that the cavity electron-ion interaction can be taken to be of the form,

$$V(s_j) = Z_j / s_j + \sum_{n=1}^{N} (c_n / s_j) \exp(-\alpha_n s_j),$$

where $Z_j = -1$ for a cation and $Z_j = +1$ for an anion. $s_j$ is the
distance from ion \( j \) to the cavity electron. If \( N = 1 \) in equation 31, then \( c_1 \) and \( \alpha_1 \) for a cation are taken from the work of HK, and for the anion they are taken from the work of Thommen. For any other value of \( N \), \( c_n \) and \( \alpha_n \) are taken from the work of KF.

The ion-ion interaction in this model are taken as the BMH-TF potential discussed in Chapter I, part E. Table 5 is a listing of the Tosi-Fumi parameters for this potential for the salts in this study.

This approach to the description of the physical properties of the solvated electron in molten salts is not the only one. In the next section two approaches are sketched.
Table 4.
A List of the Cavity
Electron-ion Potential Parameters.a

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>$a_n$</th>
<th>$c_n$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>1</td>
<td>1.072</td>
<td>1.826</td>
<td>118</td>
</tr>
<tr>
<td>K(^+)</td>
<td>1</td>
<td>0.898</td>
<td>1.989</td>
<td>118</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>1</td>
<td>0.61</td>
<td>0.90</td>
<td>120</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>1</td>
<td>0.56</td>
<td>0.90</td>
<td>120</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>$a_n$</th>
<th>$c_n$</th>
<th>Ref.</th>
</tr>
</thead>
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<td></td>
<td>2</td>
<td>4.220</td>
<td>-88.128</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.385</td>
<td>451.555</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.217</td>
<td>-391.859</td>
<td></td>
</tr>
<tr>
<td>K(^+)</td>
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<td>1.609</td>
<td>37.239</td>
<td>124</td>
</tr>
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<td></td>
<td>2</td>
<td>2.496</td>
<td>-89.970</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.201</td>
<td>87.802</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.805</td>
<td>-65.601</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>33.721</td>
<td>-72.348</td>
<td></td>
</tr>
<tr>
<td>Cl(^-)</td>
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<td>1.559</td>
<td>-16.335</td>
<td>124</td>
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<td>2</td>
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<td></td>
<td>3</td>
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<td>-702.641</td>
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<td></td>
<td>4</td>
<td>8.832</td>
<td>666.349</td>
<td></td>
</tr>
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</table>

a. All entries are in atomic units.
Table 5.
A Listing of the Parameters
for the BMH-TF Potential.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Melt</th>
<th>$A_{ij}$\textsuperscript{b}</th>
<th>$\sigma_i + \sigma_j$</th>
<th>$C_{ij}$</th>
<th>$D_{ij}$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ +</td>
<td>9.691</td>
<td>4.42</td>
<td>1.76</td>
<td>2.99</td>
<td>1.669</td>
</tr>
<tr>
<td>+ -</td>
<td>7.753</td>
<td>5.21</td>
<td>11.70</td>
<td>51.90</td>
<td>1.669</td>
</tr>
<tr>
<td>- -</td>
<td>5.815</td>
<td>5.99</td>
<td>121.19</td>
<td>869.00</td>
<td>1.669</td>
</tr>
<tr>
<td>NaBr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ +</td>
<td>9.691</td>
<td>4.42</td>
<td>1.76</td>
<td>2.99</td>
<td>1.556</td>
</tr>
<tr>
<td>+ -</td>
<td>7.753</td>
<td>5.45</td>
<td>14.60</td>
<td>70.90</td>
<td>1.556</td>
</tr>
<tr>
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<td>5.815</td>
<td>6.48</td>
<td>205.00</td>
<td>1680.00</td>
<td>1.556</td>
</tr>
<tr>
<td>KCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ +</td>
<td>9.691</td>
<td>5.53</td>
<td>2.54</td>
<td>89.50</td>
<td>1.570</td>
</tr>
<tr>
<td>+ -</td>
<td>7.753</td>
<td>5.76</td>
<td>50.20</td>
<td>272.00</td>
<td>1.570</td>
</tr>
<tr>
<td>- -</td>
<td>5.815</td>
<td>5.99</td>
<td>130.00</td>
<td>933.00</td>
<td>1.570</td>
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<tr>
<td>KBr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ +</td>
<td>9.691</td>
<td>5.53</td>
<td>2.54</td>
<td>89.50</td>
<td>1.580</td>
</tr>
<tr>
<td>+ -</td>
<td>7.753</td>
<td>6.01</td>
<td>62.70</td>
<td>369.00</td>
<td>1.580</td>
</tr>
<tr>
<td>- -</td>
<td>5.815</td>
<td>6.49</td>
<td>215.00</td>
<td>1750.00</td>
<td>1.580</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All entries are in atomic units.
\textsuperscript{b} All $A_{ij}$ entries have been multiplied by $10^3$. 
B. ALTERNATE APPROACHES

In view of the long-range of the charge-charge interaction between ions a large number of ions must be considered in the range of the cavity electron. However, this large number of ions makes a realistic a priori calculation untenable. If we are willing to compromise on a small number of reasonably placed neighbors (a "cluster"), then a Hartree-Fock type calculation can be done and a few points on the potential energy surface can be found. This is the approach of the last part of this study and will be discussed in detail there.

As a next approximation, the natural model to choose, if one wishes to include the interactions of the extra electron with the bulk medium, would be one based on the bulk properties of the medium treated as a continuum. This part of the model would account for the long-range polarization interactions. The short-range interactions between the extra electron and the electrons of the first or possibly the second model would be semi-continuous in nature in that the near neighbors would accurately reflect the structure of the local environment of the cavity electron and the continuum would account for the polarization which arises in the medium due to the charge localization.

This type of model would be a natural first choice since it has been successfully applied to polar media. \textsuperscript{71,125,126} If we adopt the same polaron models as used in polar fluids, this approach would characterize the interaction of the extra electron with a continuous medium by its static and optical dielectric constant. The optical dielectric constants of a few molten salts are available in the
literature, but there are no static dielectric constants available. The temperature dependence of the dielectric constant of a few crystalline alkali halides has been reported, but due to experimental difficulties measurements could not be done beyond the melting point.

This lack of data requires that any model proposed must rely on other measurable properties of the ions or bulk properties of the salts and on the results of the computer simulations of the molten alkali halides, as outlined in part A of this chapter.
C. PRESENTATION OF THE MODEL

In section A of this chapter we have seen how the potential well of the cavity is determined by the number of ions, by their position and by their charge distribution. What was not discussed was the importance of the overall symmetry of the local environment on the states of the cavity electron. The number of ions and their positions are important aspects because they determine the symmetry of the wave function of the cavity electron and hence the states of this electron.

For the moment let us assume that on the first coordination sphere around the cavity electron there are \( N (N = 4, 5, 6) \) metal ions. When this study was begun the organization of the second layer was not clear. One point must be made clear, in order to balance the \( N \) positive charges of the metal ions there must be an excess of \( N \) halogen ions present in the remainder of the fluid. A cluster containing only metal ions is very unstable, therefore halogen ions are included on the next layer. We take the number of halogen ions on this next layer to be the same as the number of metal ions on the first layer. With the inclusion of the halogen ions on this next layer, the cluster was found to be stable when the halogens were placed in several "reasonable" positions. The only problem remaining was that of determining the "best" place for them. Their purpose is to approximate (mimic) the interaction of the excess electron with the rest of the fluid. We assume that a reasonable constraint on their distance from the metal ions is to set this distance equal to the first peak distance in \( g_+ (r) \). Many calculations were done under this constraint to determine the "best" angular position of the
halogen ions with respect to the metal ions in the sense that we wish to minimize $E_{t}^{ls}$. With this constraint we find that the most stable position for the halogen ions is directly behind the metal ions and in line with the localization (cavity) center. Once this is established, the definition of the first coordination sphere should be changed. In what follows we define the first layer coordination sphere to be these $N (N = 4, 5, 6)$ ion pairs which are oriented with their "dipole" along the molecule-cavity center vector. The idea that the ion pairs act as weak dipoles seems justified in view of the results of the computer simulations where changes in $g_{+_{-}} (r)$, as the temperature is increased through the melting point, are interpreted as indicating the incipient formation of the ion pairs (dipoles).

In this simple model only one coordination sphere is considered and the influence of the rest of the fluid on the ion pairs is assumed to be included in this model. The distance between the ion pairs, $D$, is taken equal to the first peak distance in $g_{+_{-}} (r)$. These values are given in table 6. Use of this parameter to minimize the total energy seems unjustifiable, since the dipoles would be expanding against a vacuum rather than against the bulk of the fluid, as in the real fluid.

We have included in the potential a term, $V_{o}$, which represents the interaction of the cavity electron with the medium. $V_{o}$ represents a sum of terms. One part is the long-range screened attractive polarization interactions and another part is the short-range repulsive interactions arising from exclusion forces. $V_{o}$ then can be positive or negative depending on which terms dominate. Furthermore, $V_{o}$ is the energy of the quasi-free electronic state. In this state the extra electron is not localized in a cavity and so it "sees" a large
Table 6. Values of the Crystal Electron Affinities and of Melt First Peak Distances in the RDF.

<table>
<thead>
<tr>
<th>Salt</th>
<th>W (eV)</th>
<th>RDF peak (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.8a</td>
<td>2.80d</td>
</tr>
<tr>
<td>NaBr</td>
<td>b</td>
<td>3.05c</td>
</tr>
<tr>
<td>KCl</td>
<td>0.7a</td>
<td>3.10d</td>
</tr>
<tr>
<td>KBr</td>
<td>0.7a</td>
<td>3.35c</td>
</tr>
</tbody>
</table>

a. Ref. 132  
b. No experimental value available - assumed equal to the NaCl value.  
c. Ref. 135  
d. Ref. 136
number of medium electrons. Based on this we assume that when the localized electron is far from the cavity, it interacts with the medium in this quasi-free manner.

$V_0$ is a very difficult quantity to measure in liquids, and in the absence of any experimental data for $V_0$ in molten salts we take $V_0$ numerically equal to the negative of the electron affinity for the corresponding ionic crystal. The electron affinity of a crystal is defined as the negative of the energy of an electron at the bottom of the lowest conduction band relative to the vacuum level. The justification for using the negative of the electron affinity in crystals for $V_0$ in the melts is that the physical properties are the same even though the physical states are slightly different (mainly due to density changes). One set of values used for $V_0$, the crystal values, were taken from Hiraoka and Hamill and are given in table 6. To get more reasonable values of $V_0$, we can correct the crystal $V_0$ value for the change in density on melting. This is done in the next paragraph and the changes in $V_0$ will be shown to be small.

$V_0$ can be corrected for the change in density on melting if we assume that the work of Cohen, Jortner and Springett can be applied to ionic melts. $V_0$ is given as the sum of the kinetic energy, $T$, which accounts for multipole scattering effects, and an attractive interaction, $U_p$, due to the long-range high-frequency polarization effects, i.e.

$$V_0 = T + U_p,$$  

where the polarization energy is

$$U_p = -\frac{3ae^2}{2\pi^4} \left(\frac{8}{7} + \left(1 + \frac{8\pi\rho}{3}\right)^{-1}\right).$$
α is the polarizability, ρ the number density of the liquid, and

\[ r_s = \left( \frac{3}{4\pi \rho} \right)^{1/3}, \tag{34} \]

which corresponds to the Wigner-Seitz (W-S) radius. The repulsive short-range contribution is

\[ T = \frac{\hbar^2 K^2}{2m}, \tag{35} \]

where \( m \) is the electron mass and the wave vector \( K_0 \) is determined from the W-S boundary condition

\[ \tan K_0 (r_s - a) = K_0 r_s, \tag{36} \]

where the Hartree-Fock short-range potential of the ion-pair is assumed to be represented by a hard-core radius \( a \). Thus \( a \) can be determined from the known crystal data, i.e. from \( \rho, \alpha, V_0 \). Then using this value of \( a \) and the melt data for \( \rho \) we can calculate a density corrected \( V_0 \) for the melt. The results are given in table 7. Notice that the change in \( V_0 \) from the crystal value is small and not much larger than the estimated accuracy of the above formulas.

The total energy of state \( i \), \( E_t^i \), of the system is written as two terms. One term is the electronic contribution \( E_e^i \) and the other is the medium contribution \( E_m^i \), so that

\[ E_t^i = E_e^i + E_m^i. \tag{37} \]

The second term in equation 3 involves the sum over all the ions plus the surface tension work or its microstructure equivalent. This work is taken as

\[ E_{st} = 4\pi R_v^2 \sigma, \tag{38} \]
Table 7. Values of $V_o$ Corrected for Changes in Density on Melting.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_m$</td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>(Å)</td>
</tr>
<tr>
<td>NaCl</td>
<td>30.1</td>
</tr>
<tr>
<td>KCl</td>
<td>40.3</td>
</tr>
<tr>
<td>KBr</td>
<td>47.9</td>
</tr>
</tbody>
</table>


where \( R_v \) is the radius of the void (Figure 4) and \( \sigma \) is the surface tension of the molten salt. The values for \( \sigma \) were taken from Bloom and given below in units of dyne cm\(^{-1}\) as a function of temperature in °C.

- NaCl: \( \sigma = 190.8 - 0.093T \)
- NaBr: \( \sigma = 145.1 - 0.061T \)
- KCl: \( \sigma = 155.2 - 0.073T \)
- KBr: \( \sigma = 142.2 - 0.072T \)

then \( E_m^i \) can be written as

\[
E_m^i = \sum_{i,j}^N N \phi_{II}(r_{ij}) + 4\pi R_v^2 \sigma ,
\]

where \( \phi_{II}(r_{ij}) \) is the BMH - TF potential discussed earlier. The "dipole" distance \( D \) is not a function of the cavity radius, therefore these terms \( (r_{ij} = D) \) are not included in \( E_m^i \). This is the meaning of the prime on the summation in equation 39.

The cavity electron wave functions, \( \psi_i(r) \), of state \( i \) are taken as

\[
\psi_{1s} = \left( \frac{\zeta}{\pi} \right)^{1/2} \exp(-\zeta r)
\]

and

\[
\psi_{2p} = \left( \frac{\zeta^5}{\pi} \right)^{1/2} r \cos\theta \exp(-\zeta r),
\]

where \( r \) is the distance from the cavity center and \( \theta \) is the angle between the z-axis and \( r \). The orbital exponents are variationally determined by solving

\[
(-\hbar^2 \nabla_r^2 + V'(s)) \psi_i(r) = E_{e}^i (R) \psi_i(r)
\]
for a given cavity radius $R$, and where

$$V'(s) = V(s) \text{ for } r < R$$  \hspace{1cm} (43)$$

and

$$V'(s) = V(s) + V_0 \text{ for } r > R.$$  \hspace{1cm} (44)

$V(s)$ is the cavity electron-ion interaction potential and is given by

$$V(s) = \sum_{j}^{2N} V(s_j),$$  \hspace{1cm} (45)

where

$$V(s_j) = \frac{Z_j}{s_j} + \sum_{n}^{N} C_n/(s_j) \exp(-\alpha_n s_j)$$  \hspace{1cm} (46)

and where $s_j$ is the distance from ion center $j$ to the cavity electron.

$N$ is the number of cations (or anions) and the sum up to $2N$ means that this sum runs over all the ions of the first coordination sphere. The parameters $C_n$ and $\alpha_n$ in this potential have already been discussed in section A of this chapter and are given in table 4.

The optimum cavity size $R^i_o$ is determined, according to the stability criterion, by minimizing the total energy so that

$$\frac{\partial E^i_t(r)}{\partial R} = 0.$$  \hspace{1cm} (47)

The vertical excitation energy, $\Delta E = \hbar \nu$, is then given by

$$\Delta E = E^{2p}_{t}(R^i_o) - E^{ls}_{t}(R^i_o),$$  \hspace{1cm} (48)

and is identified with the absorption maximum of the molten salts as discussed in Chapter I, section E.
Proceeding in the usual way from equation 42, one obtains

\[ E^i_e (r) = T^i_e + \langle \psi_i^\dagger (r) | V'(s) | \psi_i (r) \rangle, \]  

(49)

where \( T^i_e \) is the kinetic energy of the cavity electron for state \( i \) and is given by

\[ T^{1s}_e = \frac{\xi^2}{2} \quad \text{and} \quad T^{2p}_e = \frac{\alpha^2}{2}. \]  

(50)

One further substitution is necessary to bring out the significance of \( V_o \). After substituting for \( V^i (s) \) (equations 43 and 44) into equation 49 the second term yields

\[ \langle \psi_i^\dagger (r) | V'(s) | \psi_i (r) \rangle = \sum_j 2N \langle \psi_i^\dagger (r) | V(s_j) | \psi_i (r) \rangle + V^i_{VE}, \]  

(51)

where

\[ V^i_{VE} = V_o (1-C_i), \]  

(52)

and where

\[ C_i = \int_{r=0}^{r=R} \psi_i^\dagger (r) \psi_i (r) d\tau, \]  

(53)

\( C_i \) is the charge enclosed in the cavity. The first term in equation 51 is the sum \( j \) over all the ions on the first coordination layer for state \( i \). The integrals in the summation are two-center integrals because the wave function is located at the cavity center and the ions are located at site \( j \). These integrals were solved in the usual way. After a rotation to align the ion center along the axis of integration, separation of variables occurs in prolate spheroidal coordinates and closed form expressions for all the integrals are obtained. The
FORTRAN program which was written to evaluate the integrals is included as the appendix. The integrals for the ls state are done in subroutine VOL1S and those for the 2p state are done in subroutine VOL2P.

The electronic energy results for this model are shown in tables 8 and 10. Since the exact values of $V_0$ or $N$ are not known, these calculations were performed for several values of these quantities. For $N = 4$ the cation centers form a tetrahedron with the anions of the "dipole" located a distance $D$ (table 6) from the cation along the radius vector from the center of the cavity to the cation. For $N = 5$ the cation centers form a trigonal bipyramid with the anions of the "dipole" located on the radius vector as above. For $N = 6$ the cation centers form an octahedron with the anion of the "dipole" located on the radius vector as above.

The medium and total energy results for this model are shown in tables 9 and 11. The quantity $E_D$ of table 9 and table 11 is the medium energy contribution when $r_{ij} = D$ in equation 39 and is given by

$$V_{ED} = N\phi_{\infty}(d).$$

(54)

Since $V_{ED}$ is not a function of $R$ it is not added into $E_D$. The other entries in table 9 and table 11 are the total medium energy contributions from $\phi_{II}(r_{ij})$ for the remaining terms in equation 17, and are given by

$$V_{CCT} = \sum_{i,j}^{N,N_1} \frac{(Z_iZ_j)}{r_{ij}},$$

(55)

$$V_{BMR} = \sum_{i,j}^{N,N_1} A_{ij} \exp \left( B(\sigma_i + \sigma_j) - r_{ij} \right),$$

(56)
and

$$V_{ST} = 4 \pi R_v^2 \sigma \quad (58)$$

Thus

$$E_m^i = V_{CCT} + V_{BMR} + V_{VW} + V_{ST} \quad (59)$$

Table 9 shows that the lowest ground state energy for each salt studied is negative. From this we conclude that the most stable state for the excess electron is the localized state in the four salts studied. The excess electron is trapped in the potential well created by the surrounding cluster of ions. Furthermore, the most stable cavity is the one with four dipole oriented cation—anion pairs for the most negative $V_0$. The stabilization is primarily due to the net attraction of the cavity electron with the cations. The energy of the charge-charge repulsions of the cavity electron with the halogen ions is about half the magnitude of the energy of its attractions with the alkali metal ions. Even though the net electronic anion interaction is repulsive the halogen ions are required for a stable cavity. The magnitude of the energy due to the repulsive term in the pseudopotential is less than 10% of the energy from the charge-charge term.

Note the trend in table 9 for $E_t^{1s}$ is one of decreasing cavity stability with increasing $N$. While no $N = 8$ calculations are reported in table 9, some $N' = 8$ calculations were done. For example, for NaCl, $N = 8$, the cavity is unstable with $E_t^{1s} = +0.2156$. This is a
Table 8. Electronic Energy Results of this Model for the Most Stable Cavity
Using the Pseudopotentials of Hellmann and Kassatotschkin.\(^a\)

| \(N\)  | \(V_0\) | \(R_{ls}^{1s}\) | \(\zeta\) | \(C_{ls}^{1s}\) | \(v_{E ls}^{1s}\) | \(E_{ls}^{1s}\) | \(\alpha\) | \(C_{2p}^{2p}\) | \(v_{E 2p}^{2p}\) | \(E_{2p}^{2p}\) | \(\text{calc}\) | \(\text{exp}\) |
|------|--------|----------------|--------|-------------|----------------|---------|------|--------|----------------|---------|---------|-------|-------|
| NaCl | T=810\(^0\)C |
|      | 0.0    | 5.15           | 0.390  | 0.93        | 0.0            | -0.2421 | 0.487 | 0.84   | 0.0            | -0.1501 | 2.503  | 1.676 |
|      | -0.029 | 5.11           | 0.379  | 0.74        | -0.756         | -0.2516 | 0.472 | 0.53   | -1.387         | -0.1647 | 2.366  |
|      | -0.031 | 5.11           | 0.378  | 0.74        | -0.805         | -0.2520 | 0.471 | 0.53   | -1.473         | -0.1655 | 2.356  |
|      | 0.0    | 6.45           | 0.348  | 0.83        | 0.0            | -0.2419 | 0.449 | 0.69   | 0.0            | -0.1767 | 1.772  |
|      | -0.029 | 6.42           | 0.338  | 0.81        | -0.566         | -0.2488 | 0.435 | 0.66   | -1.012         | -0.1874 | 1.671  |
|      | 0.0    | 7.72           | 0.314  | 0.95        | 0.0            | -0.2346 | 0.406 | 0.90   | 0.0            | -0.1784 | 1.531  |
|      | -0.029 | 7.70           | 0.304  | 0.85        | -0.453         | -0.2398 | 0.393 | 0.72   | -0.818         | -0.1868 | 1.443  |
Table 8. Continued

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|       |       | -0.026   | 5.83  | 0.345  | 0.77   | -0.603            | -0.2179 | 0.428  | 0.56   | -1.136            | -0.1457    | 1.967 |        |
|       |       | -0.027   | 5.83  | 0.345  | 0.77   | -0.603            | -0.2183 | 0.427  | 0.56   | -1.213            | -0.1464    | 1.958 |        |
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|       | 0.0    | 7.19    | 0.323 | 0.84   | 0.0               | -0.2174 | 0.415  | 0.71   | 0.0               | -0.1607    | 1.543 |        |
|       |       | -0.026  | 7.17  | 0.313  | 0.83   | -0.449            | -0.2225 | 0.402  | 0.68   | -0.817            | -0.1690    | 1.455 |        |
| **N=6**
|       | 0.0    | 8.49    | 0.294 | 0.87   | 0.0               | -0.2157 | 0.380  | 0.77   | 0.0               | -0.1661    | 1.349 |        |
|       |       | -0.026  | 8.48  | 0.285  | 0.86   | -0.358            | -0.2194 | 0.367  | 0.74   | -0.658            | -0.1726    | 1.275 |        |
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a. All entries are in atomic units except hv as indicated.

b. Ref. 102
Table 9. Medium and Total Energy Results for the Most Stable Cavity Using the Pseudopotentials of Hellman and Kassatotschkin in $E_e^{i,a}$

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**KCl**

$T=78^\circ C$

**N=4**

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    - -0.028  5.94  -6.177  -4.294  1.334  -2.255  7.060  -8.503  -1.489
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    - -0.026  8.83  -9.266  17.14  0.196  -9.261  25.76  -2.225  2.143

a. All entries are in atomic units.
Table 10. Electronic Energy Results of this Model for the Most Stable Cavity Using the Pseudopotentials of Kubler and Friauf.\textsuperscript{a}

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a. All entries are in atomic units except as indicated.

b. Ref. 102
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Table 11. Medium and Total Energy Results for the Most Stable Cavity

Using the Pseudopotentials of Kubler and Friauf in $E_{\text{L}}^{1s}$.  

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**KC1**

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*a.* All entries in atomic units.
minimum in $E_{1s}$ in that the total energies for either slightly smaller or slightly larger cavity radii are even more positive. This fact is pointed out to still any doubts that the model has stability artificially "built into it."

Although the absorption energies reported in tables 8 and 10 often differ from the experimental values by as much as 60% the trends from melt to melt are in agreement with the observed experimental trends of table 3. Most important of the trends is the decrease in absorption maximum in going from a lighter alkali metal halide melt to a heavier alkali metal halide melt. These model calculations reproduce this trend as can be seen in tables 8 and 10.

Secondarily, there is the trend of decreasing absorption maximum in going from a lighter halide to a heavier halide for a given alkali metal. The model calculations also show this trend, but the decrease in the model calculations is less pronounced than is observed in the real melts. The minimal decrease for this halide trend is not surprising in view of our approximating the rest of the melt with a single layer of halides.

These same trends are observed in the F-center absorption spectra if we assume that the lattice parameter is roughly equivalent to our cavity radius.

We can see from tables 8 and 10 that as $C_{1s}$ and $C_{2p}$ decrease there is a decrease in the 1s to 2p transition. Thus if we could improve our calculation of this property, we might obtain better agreement with experiment. There are two ways this should be done in future calculations. First, our assumption that a single layer of ion pairs can mimic the bulk melt is far too simplistic. We can improve our descrip-
tion of the bulk melt by adding more ion pairs in the cluster. The next layer of ion pairs would also be dipole oriented but less "rigidly" constrained than in the first layer. Nevertheless, the net effect of this second layer would be to draw charge out of the cavity center because additional cations would be closer to the cavity center than their accompanying anions. Second, our approximation of the cavity electron by a single exponential wave function does not allow for a sufficiently diffuse electron density, especially in the 2p state. Any improvement, in this sense, in the cavity electron wave function would allow more charge density outside the cavity.

One can still ask the question, "How good is the present model?"

To answer this question, let us consider the differences in energy on which the alkali metal trends for a given halide are based. From table 8 the calculated difference \( h\nu_{NaCl}^{\text{max}} - h\nu_{KCl}^{\text{max}} \) for the most stable cavity is 0.398 ev and the corresponding experimental difference is 0.384 ev. These calculated and experimental quantities differ by less than 4%. We can not make a fair quantitative comparison for NaBr and KBr because \( V_0 \) for NaBr is unknown (see table 6, note b). Nevertheless, the same comparison using the values from table 10 shows that these calculated and experimental quantities differ by less than 10%.

Now let us consider the differences in energy on which the halide trends for a given alkali metal are based. From table 8 the calculated difference \( h\nu_{KCl}^{\text{max}} - h\nu_{KBr}^{\text{max}} \) for the most stable cavity is 0.049 ev and the corresponding experimental difference is 0.111 ev. These calculated and experimental quantities differ by less than 10%. Again we can not make a fair quantitative comparison for NaCl and NaBr for the same reason noted above. However, these comparisons point out that the
short-range aspects of the local environment of the cavity electron are reasonably well described by the model whereas the longer-range aspects are not and as a result give larger energies than in the experimental work.

To further pursue the question of the limitations and sensitivity of our model to various parameters, we calculated the cavity radius for which \( h\nu_{\text{Calc}} = h\nu_{\text{exp}} \), for NaCl, \( N = 4, V_o = -0.03111 \) hartrees; it is \( R_{\text{O}}^{1s} = 6.27 \) bohr. This is an increase in the radius of only 18.5\% over the corresponding value at the minimum total energy given in table 8. Even at this slightly increased radius the cavity is still stable with \( E_t^{1s} = -0.0835 \) hartrees, and the decrease in stability is only 12\% from the corresponding minimum value given in table 9. Thus slight changes in the long range interactions could have significant effect on the model.

We have also calculated the absolute minimum in the total energy with respect to variations in \( R \) and in \( D \) for KCl, \( N = 4, V_o = 0.0 \). This minimum energy is \(-0.08125 \) hartrees, and is only a 6\% increase in cavity stability over the corresponding entry in table 9. The cavity radius at this minimum \( R_{\text{OO}}^{1s} = 6.17 \) bohr an increase of only 5\% from the corresponding cavity radius, \( R_{\text{O}}^{1s} \), in table 9. The cation - anion distance at this minimum is 8.14 bohr and is a 39\% increase over the first peak distance in \( g_{\text{+}} \) (D). The \( 1s-2p \) transition energy is 1.93 ev. This is a decrease of only 7\% from the corresponding value in table 8, the experimental numbers.

From these calculations we conclude that our approximate treatment of the medium is good for such a simple model. They also support our
conclusion concerning the need to provide for a more diffuse cavity electron distribution.
D. OPTICAL PROPERTIES

The dynamic nature of the melt leads us to suspect that there are cavities of various sizes and first layer coordination numbers in the melt which contribute to the observed spectrum of the solvated electron. Kestner and Jortner have included the effects of coordination number on the line shape of the solvated electron in polar fluids, and conclude that while the contribution of the medium to the line broadening of the bound-bound \( l_s - 2p \) transition is relatively important, these effects do not produce a significant asymmetry to the high energy side of the spectrum. Furthermore, most of the line broadening arises from the spherically symmetric vibrations and not from the angular "wiggling" of the dipoles about the radius vector.

Thus even though a molten salt is not a polar fluid, the ions that form the solvation cluster of the excess could be considered as weak dipoles, leading us to suspect that by including the spherically symmetric vibrations of the anions with respect to the cations, we may produce some asymmetry to the high energy side. Therefore, we have included in our calculation the spherically symmetric vibrations through the parameter \( D \). To measure the amount of asymmetry of the line shape we define the quantity \( \sigma_h \). \( \sigma_h \) (see figure 6) is the distance from the absorption maximum on the high energy side of the line shape. Furthermore, the inclusion of the larger number of configurations allows a more accurate representation of the set of thermally accessible configurations. In our line shape calculation these thermally accessible configurations are weighted by the pair distribution function \( g_{\perp} (D) \); assuming that it is unaffected by the presence
Kubo and Toyozawa have derived a general expression for the line shape which is valid for any set of potential surfaces.

\[ F(E) = \left( \frac{|M|^2}{Z} \right) \int dX \exp \left( -\frac{U_i(X)}{kT} \right) \delta(E - U_i(X) - U_f(X)) \]  

(60)

where \( U_i(X) \) and \( U_f(X) \) correspond to the potential surfaces of the initial (1s) and the final (2p) electronic states, in our case, \( M \) is the electronic transition moment (assumed independent of coordinates), \( Z \) is the ground state partition function and \( X \) represents the set of radial coordinates \( \{R, D\} \). For the melt we write

\[ F(E) = N^O \left( \frac{|M|^2}{Z} \right) \int f(R,D) dRdD, \]  

(61)

where

\[ f(R,D) = \exp \left( -\frac{\Delta E^1s(R,D)}{kT} \right) \times 4\pi g_{+}(D) D^2 \delta(E(R,D) - \hbar\nu) \]  

(62)

and where

\[ \Delta E^1s(R,D) = E^1s_t(R,D) - E^1s_t(R_0,D_0), \]  

(63)

and

\[ E(R,D) = E^{2p}_t(R,D) - E^1s_t(R,D). \]  

(64)

\( E^0_t(R_0,D_0) \) is the absolute minimum with respect to variations in \( R \) and \( D \). \( N^O \) is a scaling factor arbitrarily chosen so that the maximum of \( F(E) \) is unity. One of the integrations can be done by transforming from configuration space to energy space, taking advantage of the delta function, to yield
\[ F(E) = N_0 \left\{ \exp \left( -\Delta E_s^{1s} (R, D) / kT \right) \right\} g_{+\; (D)} D^2 \frac{dE(R', D)}{dR} \ dD \ , \quad (65) \]

where \( R' \) is the cavity radius corresponding to the transition \( E = \hbar \nu \) for the given \( D \). The factor \( \frac{dE(R, D)}{dR} \) is the Jacobian of the transformation and was evaluated numerically using the Lagrangian interpolation polynomical of degree four relevant to using five successive data points. The numerical pair distribution function for KCl is available \(^{111} \) and the remaining integral was evaluated by a five-point Guassian quadrature.

Henry and Slichter \(^{139} \) point out that the observed line shape is \( C(E \cdot F(E)) \) rather than \( F(E) \). As in the \( F(E) \) calculation, \( C \) is determined such that

\[ C(E \cdot F(E))_{\text{max}} = 1 \ . \quad (66) \]

Figure 5 is a plot of \( F(E) \) (the curve denoted by open circles \( o \)) and of \( E \cdot F(E) \) (the curve denoted by asterisks \( * \)) versus \( E \) for KCl, \( N = 4, V_0 = 0 \).

To study the effects due to the inclusion of the spherically symmetric vibrations of the anions with respect to the cations the line shape for a fixed \( D \) was also calculated. The calculation was done by taking \( F(E) \) equal to the integrand in equation 64 and plotting it as a function of \( E \) using \( R' \) as the cavity radius corresponding to the transition \( E = \hbar \nu \) for this particular value of \( D \). The value of \( D \) chosen is first peak distance in \( g_{+\; (D)} \), and a new arbitrary scale factor is chosen so that the maximum in \( F(E) \) is unity.

This was done for KCl and NaCl. Figure 6 is a plot of \( F(E) \)
Figure 5. The calculated absorption line shape of solvated electrons in molten potassium chloride including the radially symmetric motion of the anions with respect to the cations. Numerical results are given in table 12 in the row labeled HK g++. 
Figure 6. The calculated absorption line shape of solvated electrons in molten potassium chloride due only to the radially symmetric "breathing" mode of the cavity. Numerical results are given in table 12 in the row labeled HK 0. $\sigma_h$ is a measure of the asymmetry of the line shape.
(the curve of open circles o) and of E*F(E) (the curve of asterisks *) versus E.

Table 12 is a summary of the numerical results for the line shape calculations. Entries in the salt column of this table indicate which pseudopotential is used as well as which value of V₂; e.g. HK 0 means that the pseudopotential of Hellman and Kassatotschkin was used and the 0 means that zero was used for the value of V₂. Furthermore, a C in the V₂ column indicates that the calculated value of V₂ was used and the g in this column indicates these are the results of the line shape calculation using the pair distribution function and that V₂ = 0. The next entry in the salt column is the corresponding entry from either table 8 or table 10 for E, i.e. E = hν = E₂p - E₂s.

Note that by including the spherically symmetric vibrations of the anions with respect to the cations a very slight asymmetry to the high energy side is produced, and the absorption maximum shifts to slightly lower energies than those calculated in table 8, where that effect was not included.

The calculated relative half-widths, FWHM/E_max, are 30% ± 1% and they are smaller than the experimental relative half-widths reported by Schmitt and Schindewolf. They report that the average relative half-widths for all melts is around 88% with scatter about this average from 71% to almost 100%. The average relative half-widths for the solid salts is around 18% and the scatter about this average is small.

Figure 7 is the line shape observed by Schmitt for a mixture of 25 mole per cent NaCl and 75 mole per cent KCl at 730°C. The
### Table 12. Results of the Line Shape Calculations.

<table>
<thead>
<tr>
<th>Salt</th>
<th>PP</th>
<th>V_0</th>
<th>Curve</th>
<th>E_max</th>
<th>FWHM</th>
<th>( \sigma_h )</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hv(ev)</td>
<td>ev</td>
<td>ev</td>
<td>ev</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HK</td>
<td>0</td>
<td>F</td>
<td>2.041</td>
<td>0.607</td>
<td>0.305</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.085</td>
<td>E*F</td>
<td>2.077</td>
<td>0.602</td>
<td>0.300</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>HK</td>
<td>C</td>
<td>F</td>
<td>1.920</td>
<td>0.587</td>
<td>0.293</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.958</td>
<td>E*F</td>
<td>1.955</td>
<td>0.582</td>
<td>0.286</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>HK</td>
<td>g+</td>
<td>F</td>
<td>2.068</td>
<td>0.603</td>
<td>0.280</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.085</td>
<td>E*F</td>
<td>2.068</td>
<td>0.609</td>
<td>0.317</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HK</td>
<td>0</td>
<td>F</td>
<td>2.439</td>
<td>0.728</td>
<td>0.375</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.503</td>
<td>E*F</td>
<td>2.496</td>
<td>0.725</td>
<td>0.356</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>HK</td>
<td>C</td>
<td>F</td>
<td>2.308</td>
<td>0.709</td>
<td>0.345</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.356</td>
<td>E*F</td>
<td>2.346</td>
<td>0.703</td>
<td>0.352</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>0</td>
<td>F</td>
<td>2.402</td>
<td>0.732</td>
<td>0.369</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.455</td>
<td>E*F</td>
<td>2.44</td>
<td>0.727</td>
<td>0.364</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>C</td>
<td>F</td>
<td>2.231</td>
<td>0.703</td>
<td>0.355</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.281</td>
<td>E*F</td>
<td>2.271</td>
<td>0.700</td>
<td>0.352</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7. The observed absorption line shape of solvated electrons in a mixture of 25 mole per cent NaCl and 75 mole per cent KCl at 730°C. The relative half-width is 84% and $\sigma_h/\text{FWHM}$ is 0.538.
See reference 146 for original data.
relative half-width is 84% and $\sigma_h/\text{FWHM}$ is 0.538. The small amount of
asymmetry observed in this mixture is to the high energy side and in
close agreement with the corresponding entry in table 12 of 0.52.

We conclude that, while including the spherically symmetric
vibrations of the anions with respect to the cations does produce a
slight asymmetry to the high energy, it does not account for the
observed line broadening. Also, we conclude that the line broadening
present in this calculation arises from the symmetric "breathing"
mode of the ion pairs. Even though the calculated line shapes are much
broader than those of the solid salts, they are narrower than the
observed melt relative half-widths by roughly a factor of three.
Furthermore, we conclude that other thermally accessible states must
be included to account for the observed broadening in the melts and
that those states most likely to contribute to further broadening
arise from the spherically symmetric "breathing" modes of the second
layer of ion pairs with respect to the first layer.
E. AB INITIO RESULTS

In order to compare the pseudopotential calculations on a theoretical basis we performed some preliminary calculations by a priori methods. This section describes the formulation of an ab initio calculation for the solvated electron in the limiting case of the SCF approximation. That is, we adopt the Hartree-Fock framework and approximate the many-electron wave function corresponding to the discrete cluster and the excess electron as an antisymmetric product of real occupied spin-orbitals \( \phi_i \) as in equation 20. In the H-F framework the total electronic charge density \( \rho(r) \) which includes all the electrons of the solvent cluster and the excess electron, is given by,

\[
\rho(r) = \sum_i \phi_i^2(r) .
\]  

(67)

\( \rho(r) \) can be decomposed into contributions from a spin and \( \beta \) spin electrons, denoted as \( \rho^\alpha(r) \) and \( \rho^\beta(r) \), respectively. We shall employ the spin-unrestricted H-F formalism, \(^{140}\) i.e., paired electrons are not constrained to have identical spatial orbitals. We determine \( \rho(r) \) by minimizing the following expression for the total energy of state \( i \):

\[
E_i^\Sigma (R,D) = \sum_i h_i + 1/2 \sum_{i,j} (J_{ij} - K_{ij}) + \sum_{k,l} A_{k,l} (Z_k Z_l)/r_{kl} .
\]  

(68)

In equation 68, \( A \) is the number of nuclear centers and the quantities \( h_i, J_{ij}, K_{ij} \) are the usual one-electron, two-electron coulomb, and two-electron exchange integrals summed over spin-orbitals, \(^{140}\) and where \( K_{ij} \) is nonzero only for the cases where spin-orbitals \( i \) and \( j \) have the same spin.
These calculations were accomplished by modifying GAUSSIAN 70 to handle floating orbitals (orbitals without nuclear charges at their centers) and by expanding the structure of the program to accommodate a larger number of orbitals. The tetrahedral arrangement described in section C of this chapter was assumed for the solvation cluster \((\text{NaCl})_4^-\). The parameters \(R\) and \(D\) have the same meaning as in figure 4 and \(R\) is determined by minimizing \(E_T^{1s}(R,D)\) from equation 68 with respect to \(R\).

The set of orbitals on the sodium centers and the chlorine centers were taken to be the STO-3G basis set as supplied with GAUSSIAN 70. This set of orbitals was supplemented with a single gaussian-type orbital (GTO) for the ground state \((1s)\) or with a set of 2p GTO's \((2p_x, 2p_y, 2p_z)\) for the lowest excited state of the cavity electron. Newton noted that the use of GTO's in the cavity void is preferable to the use of Slater-type orbitals (STO's) because the STO introduces spurious cusps in the cavity electron wave function. This fact has also been recognized by Feng, Ebbing and Kevan in their semi-empirical calculations on excess electrons in polar liquids. The orbital exponents of the cavity wave functions were determined by energy optimization in the ground state configuration.

The most informative total energy is not the absolute energy \(E_T^1(R,D)\) but relative energies. For example, if the neutral cluster \((\text{NaCl})_4\) represents a pre-existing arrangement in the melt with the potential for trapping an excess electron, then the difference between the energy of this neutral cluster and the charged cluster \((\text{NaCl})_4^-\) including the trapped electron should provide rough estimates of the
excess electron solvation energy. The best estimate we can provide for
this energy is found by subtracting the total energy for the neutral
cluster with the floating orbital present \((NaCl)^0_4\) from the charged
ground state cluster. From table 13 we see that this difference
predicts that the charged ground state cluster is stable by around
\(-4.38\) ev, whereas the pseudopotential model calculations predict
\(-2.53\) ev (table 9) or \(-2.45\) ev (table 10) for this configuration.
Since \(k_B T\) is 0.1 ev at the melt temperature; clearly a potential well
of this depth is stable with respect to thermal fluctuations in the
medium.

The transition energy, \(h\nu = \epsilon_{ls} - \epsilon^{2p}_l\), is the highest calculated
by any model and is even higher than the observed transition in the
\(^{29}\text{NaCl}\) crystal (2.77 ev). The only explanation we can offer, over and
above what has already been discussed, is that the STO-3G basis set is
deficient in its description of the heavy atom centers, and that our
description of the cavity electron by a single 1s or 2p orbital is
too compact in that it does not provide for sufficient "delocalization"
over the metal centers. Furthermore, no consideration is given to
any other medium energy terms. The pseudopotential model does have
such considerations contained in the \(V_0\) term.

A second calculation of this nature was done with \(D = 3.5 \text{ Å}\). This
value was chosen because it is approximately halfway between the
first peak and the following minimum in \(g_\text{++} (r)\) for sodium chloride.
These results are reported in the lower portion of table 13.

At the time this calculation was planned and modification of the
program begun, the address space of the available computer was the
limiting constraint. This constraint dictated the choice of the
Table 13. Results of the Ab Initio Calculations.

<table>
<thead>
<tr>
<th>R (Å)</th>
<th>D (Å)</th>
<th>State</th>
<th>( \zeta ) (bohr(^{-2}))</th>
<th>( E^i ) (hartrees)</th>
<th>(ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NaCl)(_4)</td>
<td>2.35</td>
<td>2.80</td>
<td>--</td>
<td>-----</td>
<td>-2457.7617</td>
</tr>
<tr>
<td>(NaCl)(_4^o)</td>
<td>2.35</td>
<td>2.80</td>
<td>1S</td>
<td>0.040</td>
<td>-2457.9007</td>
</tr>
<tr>
<td>(NaCl)(_4^-)</td>
<td>2.35</td>
<td>2.80</td>
<td>1S</td>
<td>0.040</td>
<td>-2458.0617</td>
</tr>
<tr>
<td>(NaCl)(_4^-)</td>
<td>2.35</td>
<td>2.80</td>
<td>2P</td>
<td>0.040</td>
<td>-2457.9567</td>
</tr>
<tr>
<td>(NaCl)(_4^-)</td>
<td>2.30</td>
<td>3.50</td>
<td>1S</td>
<td>0.040</td>
<td>-2457.9136</td>
</tr>
<tr>
<td>(NaCl)(_4^-)</td>
<td>2.30</td>
<td>3.50</td>
<td>2P</td>
<td>0.040</td>
<td>-2457.8137</td>
</tr>
</tbody>
</table>

a. The solvation energy.

b. The transition energy.
STO – 3G basis set. Fortunately such limitations with regard to the program are no longer a problem. The computer currently available at Louisiana State University has virtual addressing and further expansion of the program to accommodate the preferred N – 31G (N = 4, 5, 6) basis set is planned. Also, modification of the program to treat the cavity electron – medium interaction via a V₀ term in the Hamiltonian will be done.

A few qualitative comparisons between this approach and the pseudopotential approach can be made. First both approaches predict that the solvation cluster is stable and quantitatively the solvation energies only differ by a factor of two. Unfortunately the second area of qualitative comparison is the insufficiently accurate description of the extra electron with bulk medium. At this state in the development of the ab initio approach a fair quantitative comparison is not possible because of the neglect of extra electron – medium interaction in the ab initio approach.
F. SUMMARY

We have attempted to develop a microscopic model for excess electron states in fused salts and we have restricted this initial attempt to four pure salt melts. This restriction was imposed not for an theoretical reason, but was due only to the availability of experimental data. The purpose of this research was not to reproduce the experimental results. The line shapes and the absorption maxima of many pure salt melts as well as many salt mixtures have been experimentally determined by more reliable instrumental techniques. Our purpose was to reveal the important interactions leading to a stable localized ground state for these excess electrons in fused salts. We have also attempted to elucidate the nature of the first excited electronic state of excess electrons in fused salts.

Calculation of the electronic energy of the excess electron was done at two levels of approximation. First, on the one-electron level existing pseudopotentials from solid state theory were used to approximate the extra electron-ion center interactions. The solid-state (crystal) electron affinities were corrected for changes in density on melting and were used to approximate the electron medium interactions. Because of the simplicity of the one-electron model, parameters were introduced into the theory. However, in the spirit of keeping the number of adjustable parameters to a minimum, the cavity size, R, is determined by minimizing the sum of the electronic energy and the medium rearrangement energy. The model can be purged of its only adjustable parameter, D, by including a larger number of ion centers and then determining their positions by minimizing the total energy with respect to all the configurational coordinates. Essentially we
could do a molecular dynamics or a Monte Carlo calculation where one of the halide centers is replaced by the excess electron.

The one-electron treatment was rather successful in predicting and interpreting semi-quantitatively several properties of interest. For example, we determined the structural arrangement and the size of the first solvation layer of the cavity electron. We have estimated its heat of solvation, its optical excitation energy and the absorption line shape for several pure molten salts. Work is now underway to modify the program to predict these properties for some molten salt mixtures.

The second level at which a single molten salt, sodium chloride, was studied was at the many-electron level. The ab initio Hartree-Fock calculation of the absorption maximum for the bound-bound 1s-2p transition can be described as fledgling at best. This calculation also predicts a stable localized ground state for the excess electron even though the bulk medium was neglected. Since the medium interaction is expected to be attractive, a slight further increase in stability is to be expected. Contrast this situation with a similar calculation by Newton who found that the hydrated electron is not stable with respect to thermal fluctuations in the medium when the bulk interactions are neglected. At the many-electron level, we were also able to calculate the solvation energy for the extra electron in molten sodium chloride. The comparison of this solvation energy with the one calculated from the one-electron model is encouraging.

In the long view of excess electrons in fluids we see that there are essentially different reasons for excess electron localization in nonpolar, polar and ionic fluids. The factor accounting for electron
localization in nonpolar fluids is due to short-range exclusion forces. In this media the excess electron "pushes" the media out of its immediate vicinity and resides in a "bubble". This type of electron localization can occur providing that the repulsive part of the potential can overcome the long-range attractive polarization contribution.

The factors leading to electron localization in polar fluids are due to the short-range and long-range polarizations which arise as a result of the permanent dipole of the fluid molecules. In polar media the electron orients those dipoles in the first solvation layer and polarizes the fluid beyond it. The resulting configurational changes lead to an energetically stable cavity.

The factors accounting for electron localization in ionic media are due to the long-range charge-charge attraction of the extra electron with the cations. In this the electron occupies a modified anion vacancy and the net result of the rearrangement is an electronic energy state more stable than the quasi-free electronic state. The structural arrangement of the first layer in ionic media is similar to that found in polar media. The cation - anion arrangement of the first solvation layer resembles weak dipoles oriented in the same direction as in the polar media.

The two levels of calculation presented in this work share common faults. Our approximation of the cavity electron by a single exponential wave function does not allow for a sufficiently diffuse electron density, especially in the excited state. Furthermore, our description of the bulk melt can be improved by including more ion
pairs in the solvation cluster. The net effect of these improvements would be to draw electron charge density out of the cavity thus lowering the transition energy and hence improving the agreement with the experimental value.


44. G. A. Kraus, J. Am. Chem. Soc., 30, 653 (1908); 30, 1157 (1908); 30, 1323 (1908); 36, 864 (1914); 43, 749 (1921).
91. R. Hilsch, R. W. Pohl, Z. Physik, 48, 348 (1928); 57, 145 (1929); 59, 812 (1930).
92. E. Mollwo, Z. Physik, 85, 56 (1933).
103. H. Davy, Phil. Trans., 97, 1 (1807); 98, 336 (1808).
129. Private communication with Professor Uli Schindewolf, September 28, 1977. Also an extensive literature search for this data was done by the author.

141. W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, "GAUSSIAN 70", Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

142. Part of the necessary modifications were supplied by J. Oakey Noel, Department of Chemistry, University of Rochester, Rochester, N. Y. The modifications to the one-electron integral routines and the required expansion of GAUSSIAN 70 to handle a larger number of orbitals were done by the author.


145. See appendix B of reference 139.

C

DRIVER ROUTINE

IMPLICIT REAL*8 (A-H, O-Z)
INTEGER SALT, CATI, ANI
COMMON SHAPE/R(500), DE(500), E(500), ID
COMMON OLIES/SMM, SHH, SMH, FPI, SQ2, SQ3, SQ8, SIGMA, AUTOAU, B,
  AMH, CMM, DMM, AHH, CHH, DHH, AMH, CMH, DMH,
  AUTOEV, SIGMAC, FST, DII, RINC, RDHP,
  RDS, SIGA, SIGB, TEPT, AMHP, AMMP, AHHP, RH,
  SALT, ANI, CATI, MR, IXN
COMMON LOOP/AST, ZST, D, RC, RM, RD, ZINC, AINC, N, M
COMMON WORDS/ZERO, ONE, TWO, THREE, FOUR, PI
COMMON ENER/ETV, E1S, VO
COMMON RS/RDH, RM2, RM3, RM4, RMS, RD2, RD3, RD4, RD5
COMMON FIRST/XN
COMMON SUMS/CI(6), AI(6), SUMC(6), SUMD(6),
  CM(6), AM(6), AH(6), LH, LC, LM
COMMON EXPM/SW
READ (5,1001) SALT, AMHP, CMH, DMH, B
AMH=AMHP*1.0D-3
READ (5,1001) CATI, AMMP, CMM, DMM, RM
AMM=AMMP*1.0D-3
READ (5,1001) ANI, AHHP, CHH, DHH, RH
AH=AHHP*1.0D-3
READ (5,1006) LM, (AM(K), CM(K), K=1, LM)
READ (5,1006) LH, (AH(K), CH(K), K=1, LH)
READ (5,1008) TEPT, SIGA, SIGB
READ (5,1004) RINC, RDS, ZST, AST, ZINC, AINC
READ (5,1005) MR
READ (5,1017) IXN
READ (5,1006) RDHP
READ (5,1006) SW
READ (5,1006) VO
1000 FORMAT (11,9X,3(2F10.5))
1001 FORMAT (A4,6X,6F10.5)
1003 FORMAT (4F10.5)
1004 FORMAT (6F10.5)
1005 FORMAT (15)
1006 FORMAT (F10.5)
1017 FORMAT (12)
1020 FORMAT (' ',F10.5,5X,F10.5)
1021 FORMAT ('0',2X,AM(I)',10X,'CM(I)'
1022 FORMAT ('0',2X,AH(I)',10X,'CH(I)'
WRITE (6,1021)
DO 30 I=1,LM
30 WRITE (6,1020) AM(I), CM(I)
WRITE (6,1022)
DO 31 I=1,LH
  WRITE(6,1020) AH(I),CH(I)
  SMM=RM+RM
  SHH=RH+RH
  SMH=RM+RH
  ZERO=0.0DO
  ONE=1.0DO
  TWO=2.0DO
  THREE=3.0DO
  FOUR=4.0DO
  PI=4.0DO
  CALL GEOM(IH)
  FPI=PI
  SQR2=DSQRT(TWO)
  SQR3=DSQRT(THREE)
  SQR8=DSQRT(8.0DO)
  XN=DFLOAT(IH)
  SIGMA=SIGA-SIGB*TEPT
  RD=RM*RINC+RDS
  N=1000
  M=1000
  AUTOAU=1.88976200
  AUTOEV=27.81200
  CONVERT SIGMA TO AUE/AUL3 FROM DYNE/CM2
  SIGMAC=(6.2348D-7)*SIGMA
  FST=FPI*SIGMAC
  RM2=RM*RM
  RM3=RM2*RM
  RM4=RM2*RM2
  RM5=RM4*RM
  RM6=RM5*RM
  IF(IH .EQ. 4) DII=SQR8/SQR3
  IF(IH .EQ. 5) DII=SQR2
  IF(IH .EQ. 6) DII=SQR2
  IF(IH .EQ. 8) DII=TWO/SQR3
  HVEVS=1.0DO
  CALL ENERGY
  CALL LINE(MR,TEPT,RINC)
  STOP
END
SUBROUTINE ENERGY
IMPLICIT REAL*8 (A*H,Q*Z)
INTEGER SALT,CATI,ANI
COMMON/SHAPE/R(500),DE(500),E(500),ID
COMMON/OLDIES/SMM,SHH,SMH,FPI,SQR2,SQR3,SQR8,SIGMA,AUTOAU,B,
  AMM,CMM,DMM,AHM,CHH,DHH,AMH,CMH,DMH,
* AUTOEV, SIGMAC, FST, DII, RINC, RDHP, RDS, SIGA, SIGB, TEPT, AMHP, AMMP, AHHP, RH, SALT, ANI, CATI, MR, IXN
* COMMON/LOOP/AST, ZST, D, RC, RM, RD, ZINC, AINC, N, M
COMMON/WORDS/ ZERO, ONE, TWO, THREE, FOUR, PI
COMMON/RS/RDH, RM2, RM3, RM4, RM5, RD2, RD3, RD4, RD5
COMMON/ENER/ETV, E18, VO
COMMON/FIRST/IXN
COMMON/SUMS/C1(6), AI(6), SUMC(6), SUMD(6), CM(6), AM(6), CH(6), AH(6), LH, LC, LM
DO 400 J=1, MR
RD=RD+RINC
ID=J
RC=RD+RM
D=RD*RM
RD2=RD*RD
RD3=RD2*RD
RD4=RD2*RD
RD5=RD4*RD
THII=DII*RD
H=RM*THII/TWO
5T=FST*D
H IS POS, INTERSECT, ZERO=TOUCH, NEG.=SEPERATED.
IF (H .LE. ZERO) GO TO 20
THSL=24.0*PI*RM*H
ST=ST+SIGMAC*THSL
20 CONTINUE
ETV=0.0
RDH=RD+RDHP
RDH2=RDH*RDH
IF (IXN .EQ. 4) GO TO 40
IF (IXN .EQ. 5) GO TO 50
IF (IXN .EQ. 6) GO TO 60
IF (IXN .EQ. 8) GO TO 80
WRITE(6,1018) IXN
1018 FORMAT('1', '$_$$_$, STOP '$_$$_$, 83X,'IXN='I4,
*2X,'NOT ALLOWED.'))
STOP
40 STERM=6.000
RMM=DII*RD
CALL SHORT(RMM, AMM, CMM, DMM, SNM, B, EV4M, CCM, BMM, VMM, 1.000)
SUMI=STERM*EV4M
RHH=DII*RDH
CALL SHORT(RHH, AHH, CHH, DHH, SHH, B, EV4H, CCH, BMH, VWH, 1.000)
CALL SHORT(RIJ, AMM, CMM, DMM, SMM, B, EV61, CC61, BOM61, VW61, 1.000)
RIJ=TW0*RD
CALL SHORT(RIJ, AMM, CMM, DMM, SMM, B, EV62, CC62, BOM62, VW62, 1.000)
CMM=12.000*CC61+THREE*CC62
BMM=12.000*BOM61+THREE*BOM62
VMM=12.000*VW61+THREE*VW62
SUM1=12.000*EV61+THREE*EV62
RHH1=SOR2*RDH
CALL SHORT(RHH1, AHH, CHH, DHH, SHH, B, EVH1, CCH1, BOMH1, VWH1, 1.000)
RHH2=TW0*RDH
CALL SHORT(RHH2, AHH, CHH, DHH, SHH, B, EVH2, CCH2, BOMH2, VWH2, 1.000)
CCH1=12.000*CCH1+THREE*CCH2
BMH=12.000*BOMH1+THREE*BOMH2
VWH=12.000*VWH1+THREE*VWH2
SUM2=12.000*EVH1+THREE*EVH2
CALL SHORT(RDHP, AMH, CMH, DMH, SMH, B, EVMH0, CCMH0, BOMH0, VWMH0, 1.000)
RMH1=DSORT(RD2*RDH)
CALL SHORT(RMH1, AMH, CMH, DMM, SMH, B, EVMH1, CCMH1, BOMH1, VWMH1, 1.000)
RMH2=RD+RDH
CALL SHORT(RMH2, AMH, CMH, DMM, SMH, B, EVMH2, CCMH2, BOMH2, VWMH2, 1.000)
CCMH=6.000*CCMH2+24.000*CCMH1
BMH=6.000*BOMH2+24.000*BOMH1
VWMH=6.000*VWMH2+24.000*VWMH1
SUM3=6.000*EVMH2+24.000*EVMH1
ERDF=6.000*EVMH0
SUM123=SUM1+SUM2+SUM3
GO TO 90
80 RIJ=TW0*RD/SQR3
CALL SHORT(RIJ, AMM, CMM, DMM, SMM, B, EV81, CC81, BOM81, VW81, 1.000)
RIJ=TW0*SQR2*RD/SQR3
CALL SHORT(RIJ, AMM, CMM, DMM, SMM, B, EV82, CC82, BOM82, VW82, 1.000)
RIJ=TW0*RD
CALL SHORT(RIJ, AMM, CMM, DMM, SMM, B, EV83, CC83, BOM83, VW83, 1.000)
CCM=12.000*(CC81+CC82)+FOUR*CC83
BMM=12.000*(BOM81+BOM82)+FOUR*BOM83
VMM=12.000*(VW81+VW82)+FOUR*VW83
SUM1=12.000*(EV81+EV82)+FOUR*EV83
RHH1=TW0*RDH/SQR3
CALL SHORT(RHH1, AHH, CHH, DHH, SHH, B, EVH1, CCH1, BOMH1, VWH1, 1.000)
RHH2=TW0*SQR2*RDH/SQR3
CALL SHORT(RHH2, AHH, CHH, DHH, SHH, B, EVH2, CCH2, BOMH2, VWH2, 1.000)
RHH3=TW0*RDH
CALL SHORT(RHH3, AHH, CHH, DHH, SHH, B, EVH3, CCH3, BOMH3, VWH3, 1.000)
CCH1=12.000*(CCH1+CCH2)+FOUR*CCH3
BMH=12.000*(BOMH1+BOMH2)+FOUR*BOMH3
VWH=12.000*(VWH1+VWH2)+FOUR*VWH3
SUM2 = 12.000 * (EVH1 + EVH2) + FOUR * EVH3
CALL SHORT(RDHP, AMH, CMH, DMH, SMH, B, EVMH0, CCMH0, BOMH0, VWMH0, = 1.000)
PRR2 = RD2 * RDH
PRR = TWO * RD * RDH / THREE
RMH1 = DSQRT(PRR2 + PRR3)
CALL SHORT(RMH1, AMH, CMH, DMH, SMH, B, EVMH1, CCMH1, BOMH1, VWMH1, = 1.000)
RMH2 = DSQRT(PRR2 + PRR3)
CALL SHORT(RMH2, AMH, CMH, DMH, SMH, B, EVMH2, CCMH2, BOMH2, VWMH2, = 1.000)
RMH3 = RD * RDH
ARG = TWO * RD * THREE + RMH3 = TWO * SQR2 * RD * RMH3 / THREE
CALL SHORT(RMH3, AMH, CMH, DMH, SMH, B, EVMH3, CCMH3, BOMH3, VWMH3, = 1.000)
CCMH = 8.000 * (THREE * CCMH1 + TWO * CCMH2 + CCMH3 + CCMH4)
BMHH = 8.000 * (THREE * BOMH1 + TWO * BOMH2 + BOMH3 + BOMH4)
VWMH = 8.000 * (THREE * VWMH1 + TWO * VWMH2 + VWMH3 + VWMH4)
SUM3 = 8.000 * (THREE * EVMH1 + TWO * EVMH2 + EVMH3 + EVMH4)
ERDF = 8.000 * EVMH0
SUM123 = SUM1 + SUM2 + SUM3

ETV = SUM123 + ST
IP = MOD(IP, 3)
IF (IP = 1) WRITE (6, 4003)
IF (IP = 1) WRITE (6, 7002) SALH, AMHP, SMH, CMH, DMH
IF (IP = 1) WRITE (6, 7000) CATI, IXN, RM, ZST
IF (IP = 1) WRITE (6, 7001) LM, B, AMMP, SMH, CMM, DMM
IF (IP = 1) WRITE (6, 7002) ANI, IXN, RH, AST
IF (IP = 1) WRITE (6, 7003) SGA, SIGB, SIGMA, TEMP, RDHP
IF (IP = 1) WRITE (6, 7004) RDS, RINC, ZINC, AINC, VO
IF (IP = 1) WRITE (6, 4000)
FORMT = 'CAVITY', '2X, 'SIGA=', 'F10.3, '10X, 'SIGB=', 'F10.3, '9X,
* 'SIGMA=', 'F6.3, '12X
* 'TEMP=', 'F6.1, '10X, 'RDF PEAK=', 'F8.4)
FORMT = 'A4.7X, 'RDS=', 'F10.5, '10X, 'RINC=', 'F10.5, '10X,
* 'ZINC=', 'F10.5, '10X, 'AINC=', 'F10.5, '12X, 'VO=', 'F10.5)
IF (IP = 0 OR IP = 2) WRITE (6, 4001)
4001 FORMAT('0*132(1H?)
WRITE(6,7009) ERDF, RDH, RMM, RHH
WRITE(6,7005) J, RC, RD, D, RMH1, RMH2
WRITE(6,7006) CAT1, CCM1, BMH, VWM, SUM1, SUM123
WRITE(6,7007) ANI, CCH, BMH, VWH, SUM2, ST
WRITE(6,7008) SALT, CCMH, BMHH, VWMH, SUM3, ETV
7005 FORMAT('J=1, 8x, RC='*F8.4, 14x, 'RD='*F8.4, 15x, 'D='*F8.4, 
*RMH1=,'*F8.4, 12x, 'RMH2=,*F8.4)
7006 FORMAT('A4,6x, CCM=,'*G16.8, 4X, 'BM=,'*G16.8, 
*5X, 'VWM=,'*G16.8, 4X, 'SUM1=,'*G16.8, 2X, 'SUM123=,'*G16.8)
7007 FORMAT('A4,6x, CCH=,'*G16.8, 4X, 'BM=,'*G16.8, 
7008 FORMAT('A4,5x, CCMH=,'*G16.8, 3X, 'BMH=,'*G16.8,
7009 FORMAT('O,9x, ERDF=,'*G16.8, 13x, 'RMM=,'*F8.4,
*13x, 'RHH=,'*F8.4)
CALL GROUND(o1S)
CALL EXCITE(o1S)
400 CONTINUE P9SO
RETURN
END
SUBROUTINE GROUND(CAVO1S)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/SHAPE/R(500),DE(500),E(500),ID
COMMON/RS/RDH, RMM, RD2, RD3, RD4, RD5
COMMON/COND/ZST, D, RC, RM, RD, ZINC, AINC, N, M
COMMON/WORDS/ ZERO, ONE, TWO, THREE, FOUR, PI
COMMON/ENER/ETV, E15, VO
COMMON/FIRST/XN
COMMON/SUMS/C1(6), AT(6), SUMC(6), SUMD(6),
*CM(6), AM(6), CH(6), AH(6), LH, LC, LM
DIMENSION VM1(3), VM2(3), VM3(3), VM4(3), VH3(3),
*VH1(3), VH2(3), VH4(3), NN(3), XX(3), ES(3), SUMM(3), SUMH(3), ZN(3)
E100Z=1, 0D20
ES (1) = ZER0
ES(2)= ZER0
ES(3)= ZER0
Z=ZST-ZINC
DO 100 I=1, N
IJUMP=1
IF(I .EQ. N) CALL MESS(Z, ES, I, IJUMP)
IF(IJUMP .EQ. 2) GO TO 130
150 Z=ZINC
LC=LM
DO 10 ILC=1, LC
CI(ILC)=CM(ILC)
AI(ILC)=AM(ILC)
AI02=AI(ILC)/TWO
TEST=DABS(Z-AI02)
IF(TEST.LT.ZINC) GO TO 150

10 CONTINUE
CALL VOL1S(Z,ROD,VM11,VM12,VM13,VM14,0)
VSUM=VM11+VM12
SUM1SM=VSUM+VM13+VM14
LC=LH
DO 20 ILC=1,LC
CI(ILC)=CH(ILC)
AI(ILC)=AH(ILC)
AI02=AI(ILC)/TWO
TEST=DABS(Z-AI02)
IF(TEST.LT.ZINC) GO TO 150

20 CONTINUE
CALL VOL1S(Z,RODH,VH11,VH12,VH13,VH14,1)
VSUH=VH11+VH12
SUM1SH=VSUH+VH13+VH14
XKE1S=Z*Z/TWO
ZRD=Z*RD
EXR=2*ZRD
EAR=DEXP(-EXR)
POLY=(EXR*(ZRD+ONE)+ONE)*EAR
VOE=VO*POLY
E1S=XKE1S+SUM1SM+SUM1SH+VOE
L=MOD(I,3)+1
VM1(L)=VM11
VM2(L)=VM12
VM3(L)=VM13
VM4(L)=VM14
VH1(L)=VH11
VH2(L)=VH12
VH3(L)=VH13
VH4(L)=VH14
NN(L)=1
XK(L)=XKE1S
ES(L)=F1S
SUMM(L)=SUM1SM
SUMH(L)=SUM1SH
ZN(L)=Z
IF(E1S.GT.0.0) GO TO 100
DELTA=E1S-E1SOLD
IF(DELTA.LE.ZERO) GO TO 100
GO TO 130

100 E1SOLD=E1S
CONTINUE
E1SMIN=DMIN1(ES(1),ES(2),ES(3))
DO 170 K=1,3
DI=F1SMIN=ES(K)
IF(DIFS.EQ.ZERO) GO TO 180
170 CONTINUE
180 CONTINUE
IF(NN(K).EQ.1) WRITE(6,1010) I.K,ES(1),ES(2),ES(3),RD
1010 FORMAT(' ',$$$ CHECK $$$*,2X,1= ',I,2X,4K5,2X,13,2Xf
*,ES(1)= ',G16.8,2X,'ES(2)=' ,G16.8,2X,'ES(3)= ',G16.8,2X,'RD= ',G16.8)
E1S=ES(K)
E1SETV=E1S+ETV
E1D=E1SETV
Z=ZN(K)
R1S=THREE/(TWO*Z)
ZRD=Z*R
EAR=DEXP(-EXR)
P=POLY*ZRD
EAR=DEXP(-EXR)
POLY=(EAR*(ZRD+ONE)+ONE)*EAR
CẢO1S=ONE*POLY
V0E=POLY*V
WRITE(6,7009) NN(K),ZN(K),R1S,XK(K),ES(K),E1SETV
WRITE(6,7010) VM1(K),VM2(K),VM3(K),VM4(K),SUMM(K)
WRITE(6,7011) VH1(K),VH2(K),VH3(K),VH4(K),SUMH(K)
7009 FORMAT(' ',1S,1= ',I,13,3X,' $I $= ',G16.8,5X,' $E I S= ',G16.8,2X,' $E I S T V= ',G16.8,1X,' *')
7010 FORMAT(' ',1S,' $V M 1 = ',G16.8,4X,' $V M 1 2 = ',G16.8,4X,' $V M 1 3 = ',G16.8,4X,' $V M 1 4 = ',G16.8,4X,' $S U M M 1 S M = ',G16.8)
7011 FORMAT(' ',1S,' $V H 1 = ',G16.8,4X,' $V H 1 2 = ',G16.8,4X,' $V H 1 3 = ',G16.8,4X,' $V H 1 4 = ',G16.8,4X,' $S U M M H S = ',G16.8)
WRITE(6,8000) V0E
8000 FORMAT(' ',8X,'VOE1S=',G16.8)
RETURN
SUBROUTINE VOL1S(Z,RC,V1,V2,V3,V4,IFLAG)
IMPLICIT REAL*8(A-H,O-Z)
COMMOM/WORDS/ZERO,ONE,TWO,THREE,FOUR,PI
COMMOM/FIRST/XN
COMMOM/SUMS/C1(6),A1(6),SUMC(6),SUMD(6),
*CH(6),AM(6),CH(6),AH(6),LM
IF(IFLAG.EQ.1) GO TO 10
CALL VSS(Z,RC,V1,VRCI)
V1=VRO
V2=VRCI
V3=ZERO
GO TO 15
10 CALL VSS(Z,RC,VORH,VRHI)
V1=VORH
V2=VRHI
V3=ZERO
15 Z3=Z*Z*Z
EZRO=EXP(-TWO*Z*RC)
XLIM=60.0
DO 100 L=1,LC
TNUM=TWO*Z3*CI(L)
BNUM=RC*AI(L)
ZPA=TWO*Z*AI(L)
ZPA2=ZPA*ZPA
ZPAR=ZPA*RC
IF (ZPAR .GT. XLIM) GO TO 60
EZPAR=EXP(-ZPAR)
GO TO 61
60 EZPAR=ZERO
61 AR=AI(L)*RC
IF (AR .GT. XLIM) GO TO 30
EPAR=EXP(-AR)
EPAR=ONE/EPAR
DIF=(EPAR*EPAR)*EZPAR
GO TO 35
30 DIF=ER20
EPAR=ZERO
35 T1=ZPAR+ONE
TZARD=TWO*(Z+AI(L))*RC
IF (TZARD .GT. XLIM) GO TO 31
ETZARD=EXP(-TZARD)
GO TO 36
31 ETZARD=ZERO
36 BOX1=EPAR*ETZARD*T1
20 ZMA=TWO*Z*AI(L)
ZMA2=ZMA*ZMA
ZMAR=ZMA*RC
T2=ZMAR+ONE
BOX2=EPAR*EZRO*T2
TERM1=BOX1/ZPA2
TERM2=BOX2/ZMA2
TERM3=DIF*T1/ZPA2
SUMC(L)=TNUM*(TERM1+TERM2)/BNUM
SUMD(L)=TNUM*TERM3/BNUM
100 CONTINUE
V3=ZERO
V4=ZERO
SUBROUTINE VSS (Z, RD, V1, V2)
IMPLICIT REAL*8 (A-H, O-Z)
COMMON /WORDS/ ZERO, ONE, TWO, THREE, FOUR, PI
COMMON /FIRST/XN
ZRD = ZRD
TZRD = TWO*ZRD
EXPRD = EXP(*TZRD)
V1 = XN*(ONE*EXPRD*(TZRD*(ZRD + ONE) + QN£)) / RD
V2 = XN*Z*EXPRD*(TZRD + ONE)
RETURN
END

SUBROUTINE EXCITE (CAVQ1S)
IMPLICIT REAL*8 (A-H, O-Z)
COMMON /SHAPE/R(500), DE(500), E(500), ID
COMMON /LOOP/AST, ZST, D, RC, RM, RD, ZINC, AINC, N, M
COMMON /WORDS/ ZERO, ONE, TWO, THREE, FOUR, PI
COMMON /ENER/ETV, E1S, VO
COMMON /FIRST/XN
COMMON /SUMS/CI(6), AI(6), SUMC(6), SUMD(6),
* CM(6), AM(6), CH(6), AH(6), LH, LC, LM
COMMON /EXPM/SW
COMMON /FACTS/FACAM, FACBM, FACAH, FACBH
DIMENSION VM1(3), VM2(3), VM3(3), VM4(3), VH3(3),
EP(1) = 0.000
EP(2) = 0.000
EP(3) = 0.000
EPOLD = 1.000
AST = AINC
DO 300 I = 1, M
IF (I .EQ. M) CALL MESS(A, EP, I, IJUMP)
IF (IJUMP .EQ. 2) GO TO 320
A = A + AINC
LC = LM
DO 10 ILC = 1, LC
CI(ILC) = CM(ILC)
AI(ILC)=AM(ILC)
AI02=AI(ILC)/2
TEST=ABS(A*AI02)
IF (TEST.LT. AINC) GO TO 100
10 CONTINUE
CALL VOL2P(A, RD, VAM, VBM, VCM, VDM)
LC=LH
DO 20 ILC=1, LC
CT(ILC)=CH(ILC)
AI(ILC)=AH(ILC)
AI02=AI(ILC)/2
TEST=ABS(A*AI02)
IF (TEST.LT. AINC) GO TO 100
20 CONTINUE
CALL VOL2P(A, RDH, VAH, VBH, VCH, VDH)
VM21=FACAM*VAM
VM22=FACRM*VBM
VM23=FACAM*VCM
VM24=FACBM*VDM
VM25=FACAH*VAH
VM26=FACBH*VBH
VM27=FACAH*VCM
VM28=FACBH*VDM
SUM2PM=VM21+VM22+VM23+VM24
SUM2PH=VM25+VM26+VM27+VM28
XKE2=AI/A/TWO
ARD=AI*RD
EXR=EXR*EXP(-EXR)
POLY3=ARD*(EXR*(ARD*(ARD+TWO)+THREE)+6.000)+THREE
PSIRD=EXR*POLY3/THREE
VOE=VO*PSIRD
E2P=XKE2*SUM2PM+SUM2PH+VOE
L=MOD(I,3)+1
VM1(L)=VM21
VM2(L)=VM22
VM3(L)=VM23
VM4(L)=VM24
VM5(L)=VM25
VM6(L)=VM26
VM7(L)=VM27
VM8(L)=VM28
XK(L)=XKE2
SUMM(L)=SUM2PM
SUMH(L)=SUM2PH
AN(L)=A
EP(L)=E2P
NN(L)=I
IF(E2P,GT,0.0) GO TO 300
DELTA=E2P-E2POLD
310 IF(DELTA,LE,0.0) GO TO 300
GO TO 320
300 E2POLD=E2P
320 CONTINUE
E2PMIN=DMIN1(EP(1),EP(2),EP(3))
DO 350 K=1,3
350 CONTINUE
IF(NIPF,NEQ,ZERO) GO TO 351
351 CONTINUE
A=AN(K)
E2P=EP(K)
E2PETV=E2P+ETV
HV=E2P+E1S
R2P=5.0/TGW*A
ARD=A*RO
EXR=TW*A*ARD
EXR=DEXP(-EXR)
P3TRY=ARD*(ARD*(ARD+TW)+THREE)+6.0)*THREE
PSID1=EXR*P3TRY/THREE
CVO2P=ONE*PSID1
VOE=PSID1*VO
HV=HV+27.212
DE(ID)=HV
WRITE(6,7012) NN(K),AN(K),R2P,XX(K),EP(K),E2PETV
WRITE(6,7013) VM1(K),VM2(K),VM4(K),VM5(K),SUMM(K)
WRITE(6,7014) VH1(K),VH2(K),VH3(K),VH4(K),SUMH(K)
WRITE(6,7101) CAV02S,CAV2P,HV,HEV,SW
WRITE(6,8000) VOE
8000 FORMAT(‘$8X’,’VOE2P=’,G16.8)
7012 FORMAT(‘$8X’,’DE(ID)=HV’,’NN(K),AN(K),R2P,XX(K),EP(K),E2PETV’,’VM1(K),VM2(K),VM4(K),VM5(K),SUMM(K)’,’VH1(K),VH2(K),VH3(K),VH4(K),SUMH(K)’,’CAV02S,CAV2P,HV,HEV,SW’,’DE(ID)=HV’,’NN(K),AN(K),R2P,XX(K),EP(K),E2PETV’,’VM1(K),VM2(K),VM4(K),VM5(K),SUMM(K)’,’VH1(K),VH2(K),VH3(K),VH4(K),SUMH(K)’,’CAV02S,CAV2P,HV,HEV,SW’,’8X’,’VOE2P=’,G16.8)
SUBROUTINE VOL2P(A, RD, VA, VB, VC, VD)

IMPLICIT REAL*8 (A-H, O-Z)

COMMON/WORDS/ ZERO, ONE, TWO, THREE, FOUR, PI

COMMON/FIRST/XN

COMMON/SUMS/ CI(6), AI(6), SUMC(6), SUMD(6),

CM(6), AM(6), CH(6), AH(6), LH, LC, LM

AR = A * RD

AR2 = AR * AR

AR4 = AR2 * AR2

RFAC = AR4 * A / 8.0D0

CALL CALCP(A, AR, YT11, YT12, YT13, YT14, YT21, YT24, YT31, YT42)

P1 = YT11 * YT12 + 3.0D0 * (YT31 * YT24 + YT21 * YT42) + YT13 * YT14

P2 = YT21 * YT12 + YT13 * YT24 + 2.0D0 * (YT31 * YT24 + YT21 * YT42)

* +YT11 * YT42 + YT31 * YT14

VA = RFAC * P1

VB = RFAC * P2

DO 210 L = 1, LC

FAC = CI(L) * RFAC

ARGA = RD * (TWO * A + AI(L)) / TWO

ARGB = RO * (TWO * A + AI(L)) / TWO

CALL CALCP(ARGA, ARGB, XT11, XT12, XT13, XT14, XT21, XT24, XT31, XT42)

P11 = XT11 * XT12 + 3.0D0 * (XT31 * XT24 + XT21 * XT42) + XT13 * XT14

P22 = XT21 * XT12 + XT13 * XT24 + 2.0D0 * (XT31 * XT24 + XT21 * XT42)

* +XT11 * XT42 + XT31 * XT14

SUMC(L) = FAC * P11

SUMD(L) = FAC * P22

210 CONTINUE

VC = ZERO

VD = ZERO

DO 200 L = 1, LC

VC = VC + SUMC(L)

VD = VD + SUMD(L)

200 CONTINUE

RETURN

END

SUBROUTINE CALCP(AAI, BI, T11, T12, T13, T14, T21, T24, T31, T42)

IMPLICIT REAL*8 (A-H, O-Z)

COMMON/WORDS/ ZERO, ONE, TWO, THREE, FOUR, PI

AAI2 = AAI * AAI

AAI3 = AAI2 * AAI

AAI4 = AAI3 * AAI

BI2 = BI * BI

BI3 = BI2 * BI

BI4 = BI3 * BI

5990

6000

6010

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6290

6300

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6350

6360

6370

6380

6390

6400

6410

6420

6430

6440
EXA=DEXP(=AAI)
EXB=DEXP(=BI)
EXBP=DEXP(BI)
BDIF=EXBP*EXB
POLYA=AAI2+TWO*AAI+TWO
BM=ONE+BI
BP=ONE+BI
AP=ONE+AAI
BPOL2=EXBP*BM=EXB*BP
POLYBM=BI2+TWO+BI+TWO
POLYBP=BI2+TWO+BI+TWO
BPOL3=EXBP*POLYBM=EXB*POLYBP
POLYA3=AAI3+THREE*POLYA
T11=EXA*POLYA3/AAI4
T12=BDIF/HI
T13=EXA/AAI
T14=(EXBP*(-BI3+THREE*POLYBM)-EXB*(BI3+THREE*POLYBP))/BI4
T21=EXA*AP/AAI2
T24=BPOL2/BI2
T31=EXA*POLYA/AAI3
T42=BPOL3/BI3
RETURN
END
SUBROUTINE SHORT(RIJ,AIJ,CIJ,DIJ,SIJ,B,EvV,CCT,BOMAT,VWT,XFLAG)
IMPLICIT REAL*B (A=H,O=Z)
COMMON/FIRST/XN
RIJ2=RIJ*RIJ
RIJ3=RIJ2*RIJ
RIJ4=RIJ3*RIJ3
RIJ6=RIJ4*RIJ2
EXBSR=B*(SIJ+RIJ)
CCT=XFLAG/RIJ
BOMAT=AIJ*DEXP(EXBSR)
VWT=CIJ/RIJ6-DIJ/RIJ8
PHI=CCT+BOMAT+VWT
EV=PHI
RETURN
END
SUBROUTINE MESS(Z,E,I,J)
IMPLICIT REAL*B (A=H,O=Z)
DIMENSION E(3)
WRITE(6,1101)I,Z,E(1),E(2),E(3)
1101 FORMAT(/'=','$S$',STOP '$S$',EXP LIMIT EXCEEDED',2X,'I=','I4',2X,
*2X,'EXP=',F8.4,2X,'E1=',G16.8,2X,'E2=',G16.8,2X,'E3=',G16.8)
J=9
RETURN
SUBROUTINE RESET(T,Q,U,W,K)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION T(16,3,3)
R=T(K,1,1)*T(K,3,2)*T(K,3,1)*T(K,1,2)
P=T(K,1,3)*T(K,3,1)*T(K,1,1)*T(K,3,3)
DENOM=T(K,2,3)*R+T(K,2,2)*P
Q=T(K,2,2)*T(K,3,1)/DENOM
U=R/DENOM
W=T(K,1,1)*T(K,2,2)/DENOM
RETURN
END

SUBROUTINE GEOM(IXN)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/WORDS/ZERO,ONE,TWO,THREE,FOUR,PI
COMMON/FACAM,FACBM,FACAH,FACBH
DIMENSION T(16,3,3)
DIMENSION ISIGN(16),FACA(16),FACB(16)
WRITE(6,2001)
2001 FORMAT('0')
WRITE(6,2001)
LN=2*IXN
DO 411 I=1,LN
READ(5,1003) ISIGN(I),PHI,THETA,PSI
1003 FORMAT(I,3F10.5)
WRITE(6,2000) ISIGN(I),PHI,THETA,PSI
2000 FORMAT(I,2X,2X,2X,2X,F16.8)
PHI=PHI*PI/180.0D0
PSI=PSI*PI/180.0D0
THETA=THETA*PI/180.0D0
CPS=DCOS(PHI)
CPH=DCOS(THETA)
SPH=DSIN(PHI)
SPS=DSIN(PSI)
STH=DSIN(THETA)
T(1,1,1)=CPS*CPH*CTH*SPH*SPS
T(1,1,2)=CPS*SPH*CTH*CPH*SPS
T(1,1,3)=SPS*STH
T(1,2,1)=SPS*CPH*CTH*SPH*SPS
T(1,2,2)=SPS*SPH*CTH*CPH*SPS
T(1,2,3)=CPS*STH
T(1,3,1)=STH*SPH
T(1,3,2)=STH*CPH
T(1,3,3)=CTH
CONTINUE
411 DO 622 K=1,LN
A = T(K, 2, 1) * T(K, 1, 2) - T(K, 1, 1) * T(K, 2, 2)
B = T(K, 2, 1) * T(K, 1, 3) - T(K, 1, 1) * T(K, 2, 3)
C = T(K, 3, 1) * T(K, 2, 2) - T(K, 2, 1) * T(K, 3, 2)
D = T(K, 3, 1) * T(K, 2, 3) - T(K, 2, 1) * T(K, 3, 3)
DENOM = C * B - A * D
WRITE (6, 3011) K, DENOM, A, B, C, D
3011 FORMAT (6, 4G16.8)
SKIP = DABS(DENOM)
IF (SKIP .LT. 0.00001) CALL RESET(T, Q, U, W, K)
IF (SKIP .LT. 0.00001) GO TO 2765
Q = C * T(K, 2, 1) / DENOM
U = (A * T(K, 3, 1) + C * T(K, 1, 1)) / DENOM
W = A * T(K, 2, 1) / DENOM
FACA(K) = (Q * 0.01 * U) / 2.00
FACB(K) = W * W - FACA(K)
622 CONTINUE
FACAM = 0.0
FACBM = 0.0
FACAH = 0.0
FACBH = 0.0
DO 711 I = 1, LN
IF (SIGN(I) .EQ. 0) GO TO 511
FACAM = FACAM + FACA(I)
FACBM = FACBM + FACB(I)
GO TO 711
511 FACAH = FACAH + FACA(I)
FACBH = FACBH + FACB(I)
711 CONTINUE
WRITE (6, 51515) (FACA(I), I = 1, LN)
51515 FORMAT (6, 8G16.8)
WRITE (6, 51515) (FACB(I), I = 1, LN)
WRITE (6, 51515) FACAM, FACBM, FACAH, FACBH
RETURN
END
SUBROUTINE DETS(H, Y, Z, NDM)
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION Y(500), Z(500)
IF (NDM .LE. 5) 4, 1, 1
1 IF (H) 2, 5, 2
2 HH = 0.01234567 / H
YY = Y(NDM) - 4
B = HH * (-25.0 * Y(1) + 48.0 * Y(2) - 36.0 * Y(3) + 16.0 * Y(4) - 3.0 * Y(5))
C = HH * (3.0 * Y(1) - 10.0 * Y(2) + 18.0 * Y(3) - 6.0 * Y(4) + Y(5))
DO 3 I = 5, NDM
A = A + B
B = C
3 CONTINUE
$C = HH \cdot (Y(I-4) \cdot Y(I) + 8 \cdot (Y(I-1) \cdot Y(I-3)))$

$Z(I-4) = A$

$A = HH \cdot (Y(I-6) \cdot Y(NDIM-3) + 18 \cdot Y(NDIM-2) + 10 \cdot Y(NDIM-1) + 3 \cdot Y(NDIM))$

$Z(NDIM) = HH \cdot (3 \cdot Y(I-1) \cdot Y(NDIM-3) + 36 \cdot Y(NDIM-2) + 48 \cdot Y(NDIM-1) + 25 \cdot Y(NDIM))$

$Z(NDIM-1) = A$

$Z(NDIM-2) = C$

$Z(NDIM-3) = R$

RETURN

WRITE(6,7000) NDIM

7000 FORMAT(0, MR MUST BE LARGER THAN 4 IN DETS. MR = 'I4,/')

RETURN

WRITE(6,7001) H

7001 FORMAT(0, RINC CAN NOT BE = ZERO IN DETS. RINC = 'G16.8,/')

RETURN

SUBROUTINE LOCACAO(MR,EO)

IMPLICIT REAL*8 (A-H,O-Z)

COMMON/SHAPE/R(500),DE(500),E(500),ID

EO = E(1)

DO 50 I=1,MR

50 EO = MIN(E0,E(I))

WRITE(6,1000) EO

1000 FORMAT(0, E1SMIN = 'G16.8,/)
SC=XK
DO 100 I=1,MR
ARG=(E(I)-EO)/KXT
FE(I)=EXP(-ARG)/DABS(DEDR(I))
FEE(I)=FE(I)*DE(I)
SCE=DMAX1(SCE,FEE(I))
150  SC=DMAX1(SC,FEE(I))
100 CONTINUE
DO 200 I=1,MR
FE(I)=FE(I)/SC
FEE(I)=FEE(I)/SCE
DEC=DE(I)*27.21200
Y(I)=FE(I)
Y(I+MR)=FEE(I)
X(I)=DEC
XL=1.23985003/DEC
WRITE(6,1110) I,XL,R(I),FEE(I),FEE(I),DEC,DE(1),E(1),DEDR(I)
1110 FORMAT(6,1110) I,XL,R(I),FEE(I),FEE(I),DEC,DE(1),E(1),DEDR(I)
200 CONTINUE
WRITE(6,3110) SC,SCE
3110 FORMAT(6,3110) SC,SCE
READ(5,714) TITLE
714 FORMAT(5,714) TITLE
READ(5,715) PLOT
715 FORMAT(5,715) PLOT
READ(5,716) LEG1,LEG2
716 FORMAT(7A1,7A1)
DO 777 I=1,MR
K=I+MR
F(I)=Y(I)
E(K)=Y(K)
777 CONTINUE
CALL FWHM(MR,X,F,EF)
RETURN
END
SUBROUTINE FWHM(MR,X,F,EF)
DIMENSION FC502),EFC502),XFC102)
DIMENSION PFC102),PEFC102),PF(102),PEF(102)
LE=999
LF=888
10000 FORMAT('1')
WRITE(6,10000)  
Z=0.0
XL=1.0E-7
HF=.5
0=1.0
DO 100 I=1,MR  
TF=0=F(I)  
TE=0=EF(I)  
IF(TF .LE. XL) IFF=I  
IF(TE .LE. XL) IEE=I  
100 CONTINUE  
XMF=X(IFF)  
XME=X(IEE)  
MRDI=MR/2  
DO 200 K=2,MRDI  
I=MR-K  
TF1=F(I)*HF  
TE1=EF(I)*HF  
TF2=F(I+1)*HF  
TE2=EF(I+1)*HF  
TF3=F(K)*HF  
TE3=EF(K)*HF  
TF4=F(K+1)*HF  
TE4=EF(K+1)*HF  
IF(TF1 .LE. TF2 .GE. TF3 .LE. TF4 .GE.) LF=I  
IF(TE1 .LE. TE2 .GE. TE3 .GE. TE4 .GE.) LE=I  
IF(TE3 .LE. TE1 .GE. TE2 .LE. TE4 .GE.) JE=K  
IF(TE4 .LE. TE2 .GE. TE3 .LE. TE1 .GE.) JF=K  
200 CONTINUE  
WRITE(6,1000) LF,F(LF),F(LF+1),LE,EF(LE),EF(LE+1)  
DIF1=F(LF+1)-F(LF)  
DIF2=HF-F(LF)  
DIF3=X(LF+1)-X(LF)  
EL=X(LF)+DIF3*DIF2/DIF1  
WRITE(6,1000) JF,F(JF),F(JF+1),JE,EF(JE),EF(JE+1)  
DIE1=F(JF+1)-F(JF)  
DIE2=HF-F(JF)  
DIE3=X(JF+1)-X(JF)  
EH=X(JF)+DIE3*DIE2/DIE1  
XFWHM=EH-EL  
XHLF=XMF+EL  
XLFH=EH-XMF  
PCL=XHLF/XFWHM*100.0  
PCH=XLFH/XFWHM*100.0  
WRITE(6,5155)  
5155 FORMAT(0,11X,'EL',8X,'SIG L',5X,'% L',11X,'EH',8X,'SIG H',5X,* 
 'EMAX',7X,'FWHM',8X)  
WRITE(*,2000) EL,XHLF,PCL,EH,XLFH,PCH,XMF,XFWHM  
2000 FORMAT(0,2X,'F(E)',:3F10.5,' x',2X,3F10.5,','*,2X,2F10.5)  
DE1=EF(LE-1)-EF(LE)
DE2=HF-EF(LE)
DE3=X(LE-1)=X(LE)
EEL=X(LE)+DE3/DE2/DE1
DH1=EF(JE+1)-EF(JE)
DH2=HF-EF(JE)
DH3=X(JE+1)=X(JE)
EHH=X(JE)+DH3*DH2/DH1
EFWHM=EH+EHLE
XLEL=EHXMEM
PCEL+XLEL/EFWHM*100.0
PCEL=XLXL/EFWHM*100.0
WRITE(6, 2001) EEL, XLXL, PCEL, EHH, XLEL, PCELH, XME, EFWHM
N=1
DO 500 IS=1, 500, 5
PX(I)=X(IS)
PF(I)=F(IS)
PEF(N)=E(F(IS)
1010 FORMAT(' 0, 'I5, 3G16, 8)
WRITE(6, 1010) N, PX(N), PF(N), PEF(N)
N=N+1
500 CONTINUE
CALL IDENT
1100 FORMAT(' 0, 'IDENT')
WRITE(6, 1100)
CALL PLOT(3, 4, 3)
1001 FORMAT(' 0, 'PLOT')
WRITE(6, 1001)
CALL NSCALE(PX, 8.5, 100, 1, 1)
1002 FORMAT(' 0, 'NSCALE X')
WRITE(6, 1002)
CALL NSCALE(PF, 5.5, 100, 1, 1)
1003 FORMAT(' 0, 'NSCALE Y')
WRITE(6, 1003)
CALL NSCALE(PEF, 5.5, 100, 1, 1)
1004 FORMAT(' 0, 'NSCALE Y2')
WRITE(6, 1004)
CALL AXIS(2, 0, '1, 5, 5, 90.0, PF(101), PF(102))
1006 FORMAT(' 0, 'AXIS Y')
WRITE(6, 1006)
CALL AXIS(0, 0, '1, 8.5, 0., PX(101), PX(102))
1005 FORMAT(' 0, 'AXIS X')
WRITE(6, 1005)
CALL FLINE(PX, PF, -100, 1, -1, 1)
WRITE(6, 1007)
SAMPLE INPUT

KCL  7,753
K+  9.691
CL-  5.815
1   .898
1   .61
780.0 1.555
0.0552 2.055
500   .215
4   .25
5,858
1,2916
-.0.0273
145.0  .54.73561
145.0  .54.73561
45.0  .54.73561
45.0  .54.73561
135.0  .125.26439
135.0  .125.26439
135.0  .125.26439
135.0  .125.26439
F(E)=0 AND F(E)*DE=*
0*
F(E)  F(E)*DE
VITA

Clarence William Finley, Jr., the eldest son of Clarence W. and Derwen R. Finley, was born on September 1, 1943 at North Charleroi, Pennsylvania. He was educated in the Rostraver Township School System in Western Pennsylvania and was graduated from Rostraver Township High School in May 1961. He attended California State College, California, Pennsylvania and was graduated with a Bachelor of Arts in Mathematics on May 25, 1964.

During his service in the United States Army from February 1969 until November 1971, he was graduated from Field Artillery Officers Candidate School on February 20, 1970 and was promoted to First Lieutenant a year later. He received an honorable discharge upon separation.

While in the Army, he married Sandra Rae Keffer on December 27, 1969, and they have one child, Kelly Rebecca. Upon separation from the Army, he entered graduate school at Louisiana State University, Baton Rouge, Louisiana and was graduated with the Doctor of Philosophy in Chemical Physics on December 20, 1978.
EXAMINATION AND THESIS REPORT

Candidate: Clarence William Finley, Jr.

Major Field: Chemical Physics

Title of Thesis: Studies of Excess Electrons in Molten Alkali Halides

Approved:

[Signature]
Major Professor and Chairman

Carolyn H. Haramura
Dean of the Graduate School

EXAMINING COMMITTEE:

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Robert V. Hauserman

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D.K. Carpenter

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A. K. Rajagopal

Date of Examination:

December 1, 1978