ARO 12068.~~[illegible]~~-RTL
2

AD A048267

Effects of Excess Charge Density on Dielectric Breakdown of Solids

12
B.S.

FINAL REPORT

J. M. Lloyd, Jr. and P. P. Budenstein

November 10, 1977

U. S. ARMY RESEARCH OFFICE

GRANT DAHCO4 74 G 0047

AUBURN UNIVERSITY

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
⑥ EFFECTS OF EXCESS CHARGE DENSITY ON DIELECTRIC BREAKDOWN IN SOLIDS.

5. TYPE OF REPORT & PERIOD COVERED
⑨ FINAL rept.,

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
⑩ Jack M. Lloyd, Jr. [redacted] Paul P. Budenstein

8. CONTRACT OR GRANT NUMBER(s)
⑮ DAHC04-74-G-0047

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Physics Department
Auburn University ✓
Auburn, Alabama 36830

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE
⑪ 10 Nov 77
November 10, 1977

13. NUMBER OF PAGES
177 ⑫ 188p.

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA ⑱ ARO ⑲ 12068.2-RTL

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Dielectric breakdown in solids
Electric strength of solids
Molecular bond strength
Hydrogen molecular ion

405 564

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

After consideration of the available experimental evidence and an examination of the previously proposed models of electric breakdown in solid dielectrics, it appears that the model (proposed by Budenstein) for the formation of a hot, high pressure gas channel within the dielectric prior to breakdown conduction more nearly describes the conditions occurring during breakdown. This paper considers the formation of a gas within a solid dielectric under high electrical stress. A possible sequence of reactions in alkali halide materials is presented. → over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

To provide further perspective on the energetics of bond disruption (gas formation), a calculation of the ground state energy of the doubly negative hydrogen molecular ion is made. This calculation shows that this state is strongly repulsive and the calculation gives a scale of distance for electron interactions with molecular states. The ground state energies of the neutral hydrogen molecule and the He-He system are also calculated with the wavefunction chosen for the doubly negative ion as a check on the accuracy of the energy calculations and for comparison with the doubly negative ion energy. The results of these calculations are applied to the breakdown problem to show that a localized excess charge density can cause bond disruption under the proper conditions and lead to the formation of a gas within the dielectric.

EFFECTS OF EXCESS CHARGE DENSITY ON DIELECTRIC BREAKDOWN

Jack Miller Lloyd, Jr.

A Dissertation
Submitted to
the Graduate Faculty of
Auburn University
in Partial Fulfillment of the
Requirements for the
Degree of
Doctor of Philosophy

Auburn, Alabama
December 8, 1977

FOREWARD:

The work reported here is the doctoral dissertation of Jack M. Lloyd, performed under the direction of Dr. Paul P. Budenstein of the Physics Department at Auburn University. Support of the U.S. Army Research Office for one year provided impetus for the work and is gratefully acknowledged. At the end of the one-year period, only a portion of the necessary calculations had been completed. Hence we submitted at that time an "interim final report" with the intent of supplying a complete report at the completion of the effort. Thus, this represents the final report for Grant DAHCO4 74 G 0047, "Dielectric Breakdown in Solids".

ACKNOWLEDGEMENTS

Many people both within and without Auburn University have aided the author greatly in developing this paper. Discussions with E. W. Thomas of the Georgia Institute of Technology, L. G. Christophorou of Oak Ridge National Laboratory and correspondence with R. Cooper of the University of Manchester (England) were especially helpful in formulating the ideas presented here. The photographic illustrations were generously provided by a number of people: Fig. 2 is courtesy of James Davisson of the Naval Research Laboratory, Washington, D. C., the other photographic illustrations were the work of Paul Hayes and J. L. Smith at Auburn University. The graphs were done at the Computer Center at Auburn University; L. G. Willis was particularly helpful in developing techniques for obtaining adequate graphs. R. W. Guthrie was of particular help in checking the accuracy of the equations, a difficult problem under any circumstances, and W. C. Neely was most helpful on the properties of colour centers.

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Materials that conduct electrical currents very poorly even in the presence of strong electric fields are known as insulators or dielectrics. Such materials find wide use in cable insulation, high voltage standoffs, capacitors, and other components. When a dielectric material is subjected to sufficiently strong electric fields, it undergoes rapid structural changes and its conductance changes markedly. The phenomena associated with these changes are referred to as dielectric breakdown. Breakdown properties are frequently studied by constructing capacitors with two parallel planar electrodes separated by a slab of dielectric material or with one planar electrode and a second nonplanar electrode separated by a dielectric slab.

The mechanisms responsible for dielectric breakdown have received attention for over 100 years (1,2). It is useful to distinguish two principal mechanisms, thermal and electrical. Thermal breakdown generally occurs in those situations where leakage currents are large and the field is less than 10^5 V/cm. In thermal breakdown, leakage current causes a temperature rise which enhances the electrical conductivity, causing still further temperature rise, the process continuing until the dielectric burns, fractures, blisters, or otherwise loses its integrity. Thermal breakdown is generally a relatively slow process, with a time scale of many seconds. Destruction to the dielectric involves a sizeable portion of the insulator, and the associated light emission is thermal in character. No new conduction mechansim has to be hypothesized in thermal breakdown; high conductance follows from the positive temperature dependence of the conductivity with temperature and damage occurs through Joule heating, by oxidation, chemical dissociation, thermal stress, and mechanical stress.

Electrical breakdown occurs at field strengths greater than 5×10^5 V/cm. It is accompanied by formation of a localized gaseous channel that grows within a few tens of nanoseconds from inception and light is emitted characteristic of the gas in the channel. The two mechanisms, thermal and electric, compete with each other in a given material under given environmental conditions (2).

Historically, another term has also been employed in describing breakdown mechanisms, "intrinsic breakdown" (2). Intrinsic breakdown refers to the (unique) ultimate breakdown strength of a material---implying that each material has a unique ultimate strength. However, attempts to measure a unique strength have not been successful (2). Thus, the most carefully annealed single crystals do not give higher breakdown strengths than crystals with strains. Deliberately introduced impurities do not necessarally reduce breakdown strength.

The present study is concerned with the theory of breakdown in solid insulators. In Chapter II, a short review of earlier experimental observations and theoretical work will be given as background information. This review will include a discussion of a phenomenological model of Budenstein (4) which will provide the basis for the present study. Chapter III considers one aspect of this model as it might pertain to alkali halides and similar materials. Chapter IV contains the major effort of this thesis, a calculation of the ground state energy of the doubly negative hydrogen molecular ion. Chapter V considers the implications of the results of Chapter IV to the general breakdown model proposed by Budenstein, and recommendations are given for further theoretical work which needs to be done in evaluating this model.

II. BACKGROUND ON DIELECTRIC BREAKDOWN

In order to put the present study into proper perspective, it is necessary to indicate the results of previous work. There exists a copious literature on breakdown in solids, including several cogent review articles and monographs (1,7,8,9). Our review here will, of necessity, emphasize those points which relate most directly to the model we wish to investigate, and without which a proper understanding of the differences between this model and others proposed previously cannot be achieved. This review will first describe a broad range of breakdown phenomena obtained from studies of thin film and bulk samples, and will then examine the existing theories of electric breakdown.

A. Experimental Background

Dielectric breakdown occurs at field strengths of about 10^6 V/cm in homogeneous dielectrics. A statistical nature of breakdown is indicated by the wide variation in the breakdown field strength found in a given substance. Indeed, in a thin film capacitor that breaks down with isolated single hole channels, the breakdown voltage may easily vary by 100% (10). Similar variations have been observed in carefully grown, annealed single crystals of various alkali halides(11). Overlapping of the distributions of the breakdown field strengths can be expected for most homogeneous insulators, even though the materials may be structurally dissimilar.

When dielectric breakdown occurs, the dielectric changes abruptly from a nonconducting state to one in which a localized current passes through the material, the local resistivity decreasing by about ten orders of magnitude (12). The conduction process is always accompanied by local destruction of the dielectric. If the device is a thin film capacitor, the electrode material may be evaporated or blown back from the breakdown channel, and the capacitor left non-shorted. Thus multiple breakdown studies may be performed on a single sample. In a macroscopic insulator, the localized region of destruction of a breakdown becomes a high conductance gaseous path through the sample. Local removal of the electrode material does not isolate this path because surface flashover from one electrode to the gaseous channel occurs upon re-application of the field before the solid dielectric can break down in another place.

The destruction within the dielectric causes the formation of a channel through the material, extending completely through the dielectric. The channel may contain frequent branching, giving a "tree" or a "star" pattern. This pattern is especially prominent for nonuniform (point-plane) applied field geometries. In other cases, such as parallel plate geometry, a straight channel with essentially no deviations may occur, or tree channels formed, normally from the cathode side. The formation of one or the other type of channel may be polarity dependent.

The following illustrations are the most graphic manner in which the evidence of the breakdown channel may be presented. The orientation of the view is along the direction of the electric field lines in each case for Figs. 1-4. Figures 1, 3, and 4 are from thin film capacitor studies, while Fig. 2 is in a bulk sample.

In Fig. 1, the typical single-channel unbranched breakdown is illustrated. This type of breakdown is normal in thin film capacitors, where the voltage is applied relatively slowly to the capacitor. The central region is the main channel, the next region the dielectric where the upper electrode has been removed by the breakdown, and the outermost region the upper electrode. Two points of particular note appear in this photograph: Firstly, the appearance of the electrode is similar to that of an explosion cavity, with much peeling back of the electrode from the channel, and lines of metal fragments extending quite some distance from the center of the channel. Secondly, the dielectric appears to have suffered structural damage in the regions visible in the photograph.

The "star" pattern of breakdown channel occurs frequently in point-plane geometries, but can occur also in other electrode configurations. The breakdown illustrated in Fig. 2 makes the origin of the name self-evident. Although the scales of the two illustrations are different, it will be noted that the breakdown event in Fig. 1 is significantly different from that in Fig. 2. In the former, the main channel was the dominant feature, whereas the side channels are much more prominent in the latter case. The "tree" pattern of breakdown is similar to the "star", but shows more extensive side-branching and a

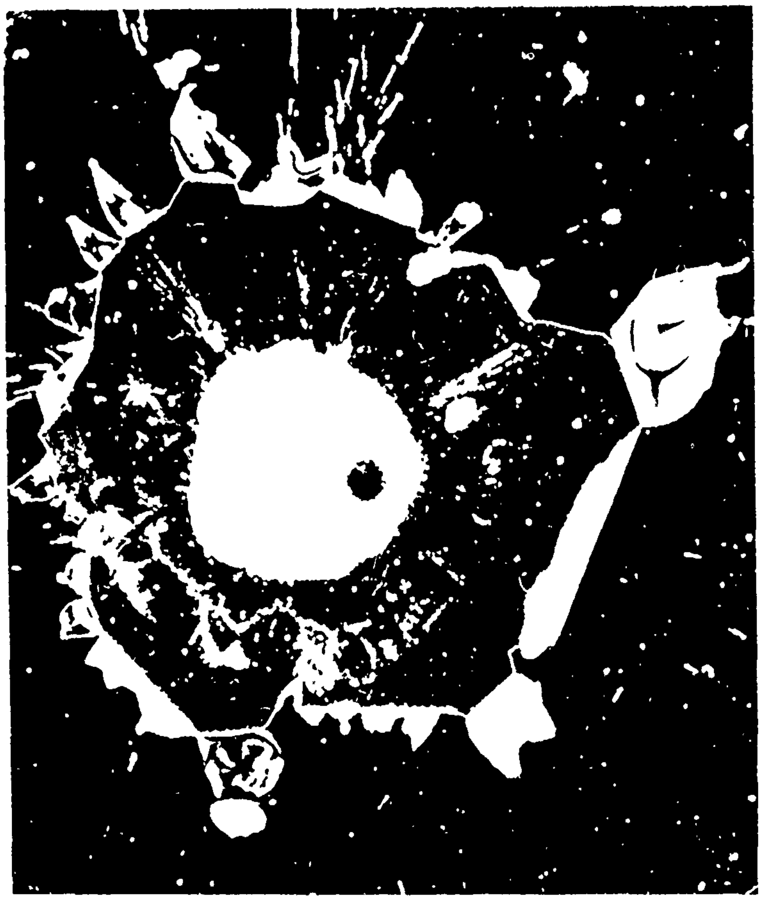


Fig. 1. Normal single channel breakdown in a thin film showing damage to dielectric and electrodes.

Fig. 2. A "star" breakdown pattern. Taken in a macroscopic sample of LiF in a nonuniform electric field.

(Photo courtesy of Dr. James Davisson, Naval Research Laboratory) much lower degree of overall symmetry in the positioning of the side channels. The "tree" pattern is not illustrated.

The next two illustrations show explicitly that breakdown channels may serve as nucleation sites for additional breakdowns in thin film capacitors. Both of these figures are somewhat atypical; the sort of clustering shown in Fig. 3 apparently occurs only in CaF_2. Clustering of breakdown channels can also occur in other materials; that of Fig. 4 is in SiO, and is the more common sort of clustering.

The process of dielectric breakdown in liquids seems to require production of a gaseous channel (13). These gaseous channels frequently exhibit a structure similar to the beading which may occur in channels in solids. A gaseous channel appears to be an essential part of the breakdown in solids. This observation is certainly compatible with the experimental observation that there exists, in thin film studies, some minimum voltage at which the breakdown event terminates. For a given capacitor, this voltage minimum is quite sharp, and seems to be the same for similar capacitors, regardless of thickness. This is explicable in terms of a gaseous discharge, which exhibits the same effect.

Examination of the breakdown region in both thin film and bulk systems provides evidence for the existence of a high pressure gas internally during the breakdown process (14). Material is thrown away from the breakdown site (as in Fig. 1), fracture lines emanate from the breakdown region, and electrodes are deformed. Inspection of the region of destruction in thin-film capacitors for a given breakdown event reveals a central region of complete destruction of dielectric and both electrodes. The outer (evaporated) electrode is further eroded or blown

Fig. 3. Multiple breakdown pattern observed in a thin-film sample of CaF_2. This type of multiple breakdown seems to occur only in this material.

Fig. 4. Multiple breakdown pattern for a thin-film sample of SiO.

back from this central region, giving a cratered appearance. The entire configuration suggests that a high pressure, high temperature gas existed in the central region during breakdown (10).

The thickness dependence of the breakdown strength has been studied for both thin films and for thicker specimens. For thin films the field strength increases as sample thickness decreases (1). A similar but less pronounced variation was observed in thicker samples (15).

Another parameter which has been studied is the temperature dependence of breakdown. It is generally found in the case of electric breakdowns that the small variation in breakdown field strength with temperature acts to lower the field strength with increasing temperature (11).

Breakdown strength increases slightly with the rate of application of voltage to the specimen (15,16). This effect seems to be found in all materials, and persists in both thin film and bulk samples.

In a study by Budenstein and Hayes (3, 17), several observations were made which relate to the most likely sites for breakdown. One observation was that, in Al-SiO-Al capacitors, imperfections with diameters of ½-1 μm were frequently the sites where individual breakdowns would occur. The identity of these defects was not discernable, however. If the beam of an electron microscope were focussed on a defect and the voltage across the capacitor gradually increased, breakdown would <u>always</u> occur at the irradiated defect. However, if none of the above defects were within the illuminated area, breakdown would occur at some other site, out of the field of illumination. The capacitors studied varied in thickness from about 2000 Å to around 10000 Å.

In another study (10), it was found that the material of the electrode made a significant difference in breakdown strength; it has also been noted that the change from metallic to electrolytic electrodes makes a considerable difference in the pre-breakdown behaviour of the capacitor (18). This may be attributable to changes in the work function at the electrode-dielectric interface. It has also been determined that the polarity of the applied voltage influences somewhat the character of the breakdown (17). The effect of polarity decreased for increasing dielectric thickness.

Studies have also been carried out which analyze the light emission produced during breakdown (10). In the case of thin film capacitors, Smith found that the spectral character of the light emitted was entirely a gaseous bright-line spectra of the electrode and dielectric materials. This study was carried out using Al-SiO-Al capacitors primarally, but similar results were obtained using Al-SiO-Cu capacitors, and capacitors with MgF_2 as the dielectric material. Neutral state and second-ionization state radiation was observed in these spectra, but the emission spectra of the singly ionized species predominated. The light emission spectra was observed within a time of about 10 nsec from the onset of breakdown conduction as indicated by the voltage waveform. A search to detect any thermal component in the radiation indicated that the thermal component was less than one percent of the total emission, if it was present at all. Another point of some significance is that when the electrodes were of different materials, the spectra of both were present from the first, in addition to that of the components of the dielectric.

Cooper and his coworkers at Manchester have also carried out a number of experiments which provide information on the breakdown transition (19,20). In the majority of their studies, the specimens used were alkali halide single crystals about 0.5 mm thick. Prebreakdown currents up to about 10^{-8} amperes occurred in samples for field strengths of about 60 percent of the breakdown value. The transit time for electrons in the samples they employed were determined to be about 5 nsec (19). In these experiments, they were able to investigate the prebreakdown light emission to within about 2 nsec of voltage breakdown. The initial intensity of the emitted light was so small that an image intensifier was required to determine the light output. This technique did not, unfortunately, allow them to determine any spectral differentiation in the light. Light emission was first detected about 20 nsec before the voltage drop characteristic of breakdown. At 19.5-20 nsec, a faint glow was detected near the cathode, extending for some distance along the cathode, but not for any great distance into the dielectric. This diffuse light gradually extended itself across the dielectric, growing somewhat in intensity. This core completely crossed the dielectric about 10 nsec before the onset of breakdown. The light emission grew rapidly in intensity from this point on. It was also observed that the light from the core region showed a beaded appearance, typical of many breakdown patterns. This core region did indeed become the breakdown channel.

From the inability of doing spectral analysis of the light, Cooper was not able to say what physical process was producing the light. From investigation of temperature variations he felt that it was not arising from thermoluminescence (22), but was from the same process as the breakdown, or from a process which was intimately connected with the formation of the breakdown channel.

Cooper et al (20) also studied the orientation of breakdown channels in single crystal samples which had been carefully annealed. The breakdown channel would, for a particular alkali halide, normally align in a simple crystallographic direction (usually [100] but [110] was occasionally observed), even when the applied field was in some other direction. A photograph is shown of a breakdown channel in KCl when the applied field was in the [110] direction. The channel started out in the [100] direction, shifted to a [010] direction, and then changed back to its original direction. Unannealed and polycrystalline samples did not exhibit this behaviour, but would break down in the direction of the applied field.

Grinberg and de Grinberg (21) report directional effects in breakdown. In this case, the breakdown channel lies predominantly in a [110] direction, with side branches in a [100] direction. No treeing or dendritic growth to the channel was noted; each side branch was single. Their crystals were, however, prepared by cleaving after annealing, and thus are not comparable with those of Cooper's work, where it was demonstrated that the presence of the strains caused by cleavage could alter the breakdown direction. Grinberg and de Grinberg also find the presence of free atomic alkali metal in amorphous form about the breakdown channel.

Another point determined by the study of Al-SiO-Al capacitors by Budenstein and Hayes (17) is of some interest in this connection.

Selected area transmission electron diffraction studies of breakdowns determined that "balls" or crystalline silicon of about 1 μm diameter were always found in the breakdown region. X-ray diffraction studies of these capacitors before and after breakdown showed that the silicon was a result of the breakdown process, and did not exist within the specimen prior to breakdown.

Similarly, in electron beam interaction studies of insulating materials, a chemical reduction of cations has frequently been observed at relatively high beam currents (23,24). In this case, the cations normally form into amorphous clusters of essentially atomically pure material in the region where the beam current is relatively large, frequently globular in shape. Also, it sometimes occurs that breakdowns occur in these samples; these breakdowns have channels similar to those of the breakdowns which occur in capacitor studies.

In another study of thin film SiO capacitors, Tsuchida and Ueda report the "breakdown strength" (for SiO films of thickness greater than about 200 Å) "increases rapidly with decreasing thickness and increased linearly with increasing work function of cathode metal, and temperature had a little effect on the breakdown strength" in the range of thickness investigated (25). For extremely thin films, they found the breakdown strength to increase somewhat for decreased thickness. For such very thin films, however, the current-voltage characteristics in the prebreakdown region are those of a Zener diode, and the conduction was characteristic of Fowler-Nordheim emission at the cathode. They concluded that breakdown in such very thin films was correctly described by Zener's model.

B. Theoretical Background

The literature dealing with the theoretical aspects of dielectric breakdown is extensive, with a number of review articles available which cover most of the major work (1,11,26). The salient points of most major earlier theoretical work will be indicated in this section, grouped by basic mechanism.

Avalanche Theories

Most current theories of breakdown in solid dielectrics begin with the assumption of electron multiplication by an avalanche process. The basic argument is that there exist conduction electrons within the dielectric capable of gaining sufficient energy from the electric field to enable them to ionize valence electrons from the atoms in their path by a scattering event. Then the "new" electrons, as well as the incident electrons, will repeat the process, and, for a sufficiently strong electric field, lead to a geometrical progression in the number of conduction electrons. It is assumed that the addition of electrons to the conduction band is the direct cause of the high currents characteristic of breakdown, and that disruption of the dielectric follows the high current by Joule heating of the material. We shall examine briefly two types of avalanche theories, one in which the applied field is the dominating factor, the other in which space charge plays an important role. Other theoretical treatments will also be considered following these.

Probably the earliest of the field-critical theories was suggested by von Hippel, and developed analytically by Callen (27,28). For a small applied field, conduction electrons do not, on the average, gain energy from the field; they remain near the bottom of the conduction band. With increasing field strength, the average energy slowly increases, but energy losses associated with scattering events still dominate. However, at a sufficiently high field strength, the energy gain between collisions is sufficient to lower significantly the collision probability. Once beyond this "friction barrier", an electron gains sufficient energy to cause secondary ionization through a collision process with a bound electron in the valence band. The friction barrier is in the range of 0.1-0.2 eV above the edge of the conduction band. The critical field for breakdown is taken to be the electric field at which the average conduction electron energy is equal to the friction barrier (1). The principal features of this treatment include:

1. The field strength necessary to cause breakdown is that field capable of accelerating the average conduction electron to ionization energy, regardless of its initial energy.
2. The breakdown field will increase with an increase in temperature. This is a direct result of the enhanced scattering at higher temperatures. Smith (15) indicates an increase in field strength in NaCl of from about 1.1 MV/cm at 0°K to 1.6 MV/cm at 500°K.
3. The field required for breakdown in independedt of thickness.

Frohlich suggested that it is not necessary for the average energy of the conduction electrons to exceed the friction barrier, but that only the highest energy electrons need be accelerated to the ionization energy (1). The critical field for breakdown under this assumption is taken to be that field at which the rate of energy lost to the lattice in a collision is equal to the rate of energy gained from the electric field for an electron at the ionization energy (1). At the critical field strength, electrons with higher initial energies will attain energies greater than the ionization energy. Thus the high energy tail of the electron energy distribution is gaining energy from the field more rapidly than energy is being lost in collisions with the lattice. We thus have a supply of electrons available to cause the avalanche multiplication of electrons. Frohlich's criterion is similar to that of von Hippel and Callen in that both predict a critical field strength that depends on an energy balance. The difference between the two is the emphasis on the status of the average conduction electron by von Hippel and Callen and on the high energy tail by Frohlich. As the field required to accelerate the average electron through the friction barrier is considerably greater than that required to accelerate the high-energy electrons through the barrier the predicted field strength of Frohlich is significantly less than that predicted by Callen's criterion. The other basic prediction of Frohlich's model which differs from that of Callen is a greater temperature dependence. Frohlich predicts a breakdown field in NaCl of 0.4 MV/cm at 0°K and of 0.8 MV/cm at 600°K (1).

The theory of Forlani and Minnaja (1) assumes multiplication of the Fowler-Nordheim emission current from the cathode. Through a consideration of current continuity obtained by equating the injection and multiplication currents, they obtain a critical field for breakdown which varies approximately as the inverse square root of the sample thickness. Their paper does not treat temperature dependence.

Zener (29) proposed an alternate electron multiplication model which was further developed by Franz (30). In this model, explicit avalanching by collisions does not play any significant role, but the field production of electrons by tunneling is taken to be the main source of conduction electrons. Once an electron has entered the conduction band, it is accelerated by the field in the direction of the anode. Since conduction electrons will be generated throughout the material, the greatest current density will occur near the anode. The critical field strength increases with the rate of application of the field and with temperature. The mechanism for the disruption of the dielectric is again Joule heating by the current.

In each of the preceding theories, the basic concept was that breakdown was an intrinsic property of the dielectric, with the breakdown conduction being determined largely by the band gap of the material. As experimental evidence relating breakdown in thin film and in bulk single crystal systems became available, these ideas became more difficult to support. In the past decade, an increasing emphasis has been placed on the statistical nature of breakdown events, reflecting the comparatively wide range of breakdown fields observed in even the most carefully prepared specimens (9). The theories which have been proposed most recently have considered the role of space charge in the breakdown process Since space charge distributions depend strongly on the specimen geometry, its past electrical history, leakage currents, and the presence of defects and mechanical strains, their variability can well account for the fluctuations observed in breakdown strengths. The following theories each consider the effects of space charge on the process, with less emphasis being placed on the occurrence of avalanching.

O'Dwyer (31-33) took the space charge into account by requiring the continuity of current, assuming that the current is carried solely by electrons. His work also included physically meaningful boundary conditions at the electrodes, including electrode injection of carriers, and modifications to the field due to the space charge. This model still considers that collisional ionization plays a significant role. The results obtained in (31) predict a sharply rising field at the cathode when the overall field exceeds some critical value. The curve obtained here requires ionization rates which are not unreasonably high; the critical field (expressed in dimensionless form) varies approximately linearly with the dimensionless inter-electrode separation. The results of (33) are much more involved, and require numerical or graphical evaluation.

Watson and Heyes (16) have considered the build-up of space charge by ionic migration to the cathode to predict the field strength for breakdown, and the dependence of breakdown field on the rate of application of the field. The critical field yielded by this treatment seems to exceed those normally accepted as bulk breakdown field strengths, but the critical field obtained by their approach is the field at the cathode. This may correspond to a critical field for the build-up of space charge near the cathode. Good agreement between theory and experiment is claimed.

DiStefano and Shatzkes (6) have considered an impact-ionization model in which the effects of recombination are taken into account. Space charge is created which enhances the field in the cathode region. Ultimately, an instability develops as electrons injected from the cathode gain energy from the field. Impact ionization of the lattice by the electrons enhances the positive space charge near the cathode, which increases the cathode field, which enhances the electron emission at the cathode, etc. In the case of SiO_2 their model predicts a current density for the instability (breakdown) which increases rapidly for films with thickness below 200 Å.

The impact ionization (avalanche) models seek to explain the observed increase in current accompanying electric breakdown. Such a current rise is taken as a necessary condition and occurs prior to any damage. Damage to the dielectric is assumed to follow the high current and to be thermal in nature. The direction of the current should be the same as the field direction. Light emission should be either a recombination radiation in the solid or a thermal emission from the solid.

Critique of Avalanche Theories

Having examined both the experimental evidence and the various avalanche theories of electric breakdown, it is now possible to summarize. The avalanche approach has several virtues, including:

1. Avalanche theories explain the large increase in current that is characteristic of breakdown.
2. They explain localization because small geometric variations can give rise to high local fields and the size of an avalanche increases greatly with electric field.
3. They explain the insensitivity of breakdown to the structure of the dielectric, since it depends only on the gross features of the electrical band structure.
4. They provide some basis for understanding the thickness dependence of the breakdown field.

Thus there are a number of points which are well covered by the avalanche theories.

However, there are significant observations that do not appear to be explicable in terms of the avalanche hypothesis. The most notable of these include:

1. Failure to account for a gaseous channel prior to the rise in current and fall in voltage indicating breakdown.
2. Failure to account for the line spectra observed from the beginning of breakdown conduction in thin film studies.
3. Failure to account for the breakdown configuration in point-plane geometries and in annealed single crystals: the channel in

these situations will follow favored crystallographic orientations rather than parallelling the electric field.

4. The nonexistence of current precursors to breakdown renders unlikely any mechanism which requires the formation of high current densities prior to the disruption of the dielectric (25).

5. Failure to account for the geometry of electrode damage in breakdowns---in an avalanche model, such damage should be primarily by Joule heating. In practice, damage is strongly dependent on the high pressure gases formed within the dielectric.

6. The chemical composition of the reaction products from a breakdown channel is not explicable in terms of thermal decomposition products, but is explicable on the assumption that the material is broken down into its separate atoms and then these atoms subsequently chemically recombine (34).

7. There does not seem to be any direct experimental evidence showing the existence of substantial avalanche current in any solid dielectric system so far investigated.

8. Breakdown occurs in thin film systems at voltages too low for the process to exist. For a field strength at breakdown of 5 MV/cm, a sample having a thickness of 500 Å will break down with an applied voltage of 25 Volts. If the insulator in question has a band gap of 10 eV, not more than two ionizations can occur per incident electron, as the electron will lose most of its energy in each collision. Thus avalanche cannot directly cause the large increase in current required in the avalanche theories of breakdown.

It might be well to use Cooper's words to summarize the state of theory and experiment at this point: "Seitz's single avalanche theory, and also other theories in which current multiplication occurs by electron avalanching and of which the theory recently proposed by Forlani and Minnaja is an example, are incompatible with the pattern of light emission" exhibited in Cooper's work (19). The article this quotation is taken from was published in 1966, but the views are those which Cooper still holds (22). Others, notably Budenstein (17), also expressed doubts about the applicability of the avalanche approach at about this same time.

Gaseous Model of Electric Breakdown

A model of breakdown in solids has been proposed by Budenstein (4,35) that attempts to account for a broader range of breakdown phenomena than seems possible with the avalanche models. The basic assumption of the model is that, in a sufficiently high electric field, breakdown in a solid occurs when a highly conducting gaseous channel is formed that bridges the electrodes. Thus the theory of breakdown must be able to explain how this conducting channel is formed. In the formation of the channel, the following sequence of steps is hypothesized:

1. The basic assumption is made that the breakdown starts when the density of excess charge in a local region containing many atoms exceeds a critical value. This charge density may be produced by any of several processes, such as field emission from the electrodes, ionization associated with the absorption of light, electron injection from a high energy electron beam, or some other means.

2. The effect of this excess charge density is the destruction of chemical bonds in the local region. When the bonds are broken, the products form a gaseous plasma containing excited atoms, ions, and free electrons. This plasma, to sustain itself within the solid, must be of high density, high pressure, and high temperature.

3. If the free electrons within the plasma are of sufficient density, so that they produce at the plasma-solid interface the critical charge density, then the process is self-sustaining.

4. As the reactions proceed, a gaseous cavity is formed within the solid. The pressures generated within the gas can lead to the formation of cracks within the remaining solid material, extending the reaction zone.

5. When the channel completely bridges the electrodes, current begins, and, in most circuits, the voltage between the electrodes falls.

III. ANALYSIS OF BOND DISRUPTION

The present study was performed to provide some insight concerning the nature of the excess charge density necessary for disrupting chemical bonds and of the energies of the released particles after bond disruption, i.e., to provide a basis for the first step in the gaseous model of electric breakdown described in Section II.3. For the gaseous model to be feasible, the excess-charge-induced reaction must be exothermic. (Conversion of a solid to a gas is normally an endothermic process. However, in the normal situation, the system is not subjected to an external electric field in the MV/cm range.) In this chapter, the energetics of the formative stages of breakdown are analyzed in two stages. The first involves energy storage within the dielectric, the second the solid-to-gas exothermic reaction. For definiteness, these will be explored in terms of a particular material, NaCl, an alkali halide, in a uniform field geometry.

A. Storage of Energy within the Dielectric

1. Generation of Defect centers by Impact Ionization

At low applied voltages, the small leakage current through a bulk dielectric arises from mobile ions and, by means of the hopping conduction mechanism, or by the Poole-Frenkel mechanism, from electrons. If there is no injection of electrons or holes at the contacts (blocking contacts), only a transient current will flow while space charge is built up at the electrodes.

As the applied voltage increases, the potential barrier at the cathode-dielectric interface can be penetrated by Schottky or Fowler-Nordheim emission of electrons into the dielectric, and a significant injection current may begin. (This occurs at field strengths less than one-tenth of the breakdown strength (36). Values for the work function at the cathode-dielectric interface do not seem to be available, but a representative value is one-half of the band gap of the dielectric (37)).

As the voltage continues to increase, the injection current increases, and some injected electrons pass through the friction barrier and attain energies sufficient to eject electrons from their bound sites. If an electron of a Cl^- atom is ejected, then a V_k colour center may be created within the dielectric. The method of production of V_k centers has been studied by Dienes (38), and their properties are described by Fowler (39), Townsend and Kelly (40), and Schulman and Compton (41).

A V_k center in an alkali halide consists of a molecular ion occupying the lattice sites of two normal halide ions, with the atoms comprising the molecule displaced from the lattice sites toward a common center. The molecular ion is usually formed from the ions originally occupying the lattice sites. A qualitative diagram of this center is given in Fig. 5. A more comprehensive discussion of this colour center, along with the H and F centers, is given in Appendix D. According to Dienes (38), the center is normally formed by ionization of one of the atomic sites, followed by a combination of the neutral atom with an adjacent ion to form a molecular ion. The latter is more stable in crystals at low electric fields than the neutral-ion configuration with each atom remaining at its original equilibrium site. The stabilization energy of the state in NaCl is about 1.4 eV, and the center forms an isolated energy level in the solid at about 6.5 eV above the valence band (38). Using the normal criterion for the incident energy to be three-halves the band gap, this would require the incident electron to have an energy of about 11.8 eV to allow the formation of this state (the band gap of NaCl is about 7.85 eV). The equilibrium separation of the nuclei in the molecular ion is about 2.3 Å, compared to 2.8 Å in the normal lattice.

Paracchini (36,42) has observed cathodeluminescence at liquid nitrogen temperatures and below for alternating fields greater than 10^4 V/cm in several alkali halides, although not for NaCl. In the case of a d.c. electric field, a space charge internally built up in the dielectric reaches equilibrium with the applied field, and luminescence is not observed. Paracchini attributes this luminescence to V_k centers created by impact ionization initiated by electrons injected from the cathode. A field of 10^4 V/cm is substantially below that required for breakdown. The cathodeluminescence is not seen at higher temperatures, as the transition is no longer radiative at higher temperatures. Paracchini finds that the centers are created predominantly in the cathode region, as indicated by the light emission pattern. For each center produced, there will be a contribution to the space charge of a positive electronic charge, as the center production process has involved the removal of an

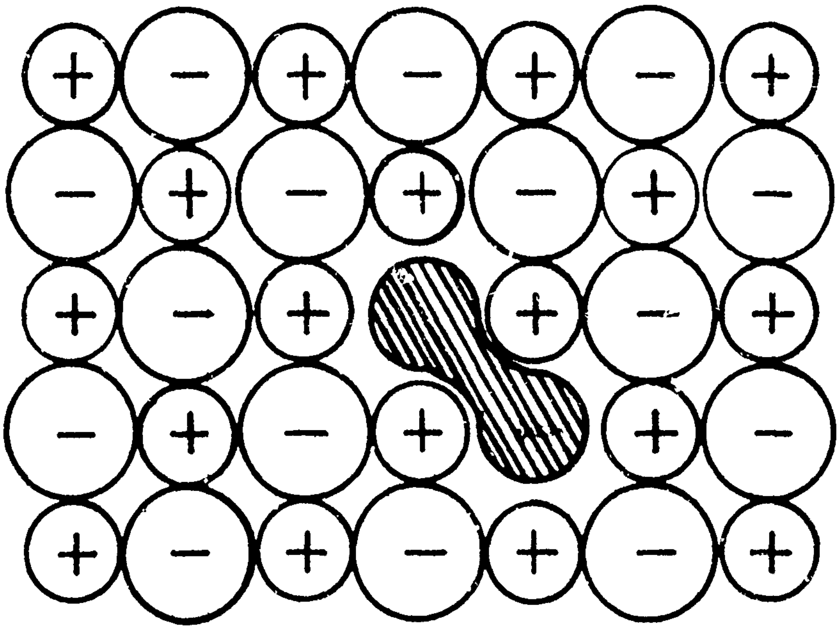


Fig. 5. Sample configuration of V_k center in alkali halide crystal. Note that the two halide atoms comprising the molecular ion occupy sites close to those of the original halide ions.
(After Townsend and Kelly)

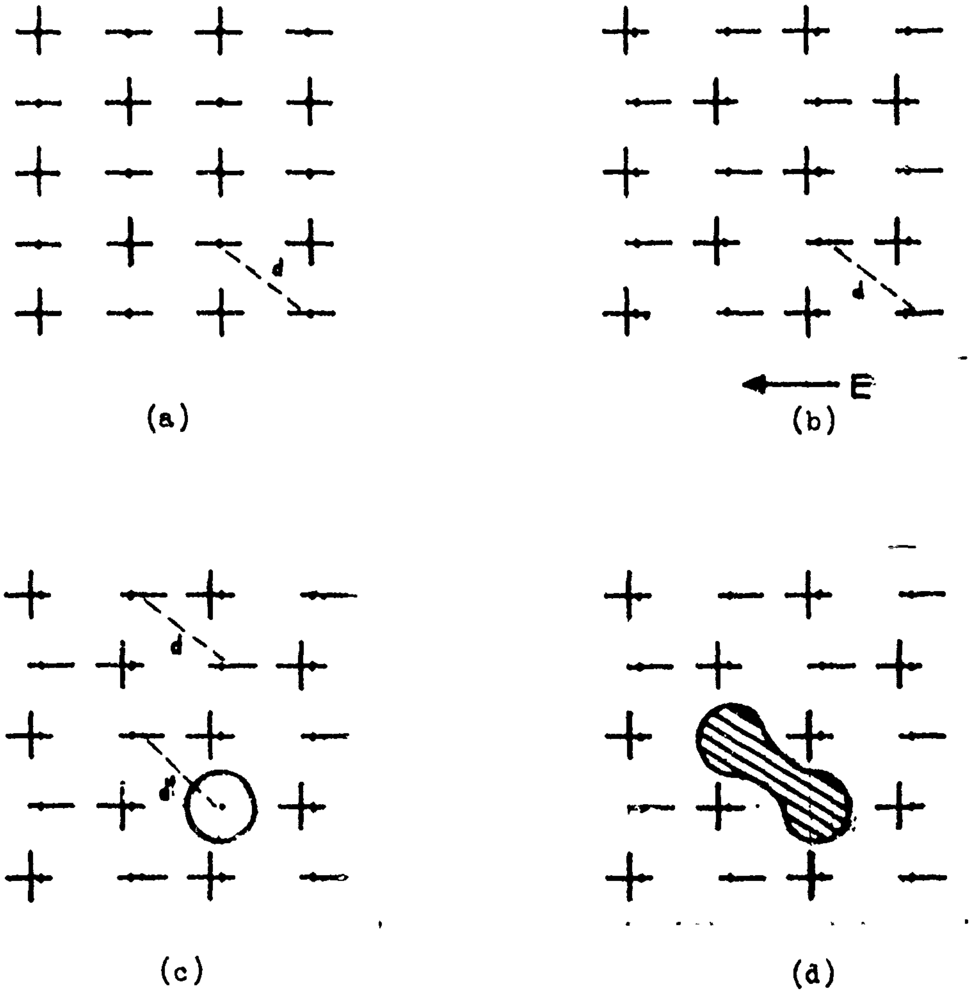


Fig. 6. The effects of polarization on the formation of V_k centers is illustrated by this sequence of drawings. (a) Shows a normal lattice. (b) Shows the shift of atomic species away from the lattice points (indicated by dots) due to the action of the electric field. The distance between halide ions is indicated by d. (c) Shows a neutralized halide atom. The distance indicated by d' is less than d. (d) Shows the V_k center formed by the neutral halide atom.

electron, leaving an unbalanced positive charge. The low temperature luminosity is due to a radiative recombination of an electron with the center.

2. Properties of Defect Centers

The production process of the V_k centers may be represented in chemical notation by the expressions

$$Cl^- + e^- + E0 \longrightarrow Cl^\circ + 2\,e^- \qquad E0=7.85\ \text{eV}$$

$$Cl^\circ + Cl^- \longrightarrow Cl_2^- + E1 \qquad E1=1.4\ \text{eV}$$

Or, we may describe the system by the single equation

$$2\,Cl^- + e^- + E' \longrightarrow Cl_2^- + 2\,e^- \qquad E' = E0-E1$$

To attain the excitation energy at which cathodeluminescence is observed requires accelerating distances in excess of 10 μm in Paracchini's experiment, and decreases to about 0.1 μm at an applied field of 10^6 V/cm.

The effect of polarization on the formation of V_k centers is illustrated in Fig. 6. The lattice positions of the crystal with no applied field are shown in Fig. 6a, where the equilibrium separation between sites is (d), the separation being about 2.6 Å. Polarization shifts the ions away from their equilibrium positions in the neutral unstressed crystal, as shown in Fig. 6b. After impact ionization has occurred at a Cl^- site, the adjacent positive ions relax by moving toward the neutral (Fig. 6c). This latter relaxation lowers the separation of the neutral and an adjacent halide ion, thus favoring the formation of V_k centers. The conditions needed for the formation of V_k centers exist in breakdown studies.

The reverse reaction is also possible:

$$Cl_2^- + e^- \longrightarrow 2\,Cl^- + E' .$$

The energy given off in the reverse reaction may appear as lattice vibrations (phonons), go into the production of paired H and F centers, or, at temperatures below 80°K, may appear in the form of visible light (38). The H center is chemically the same as the V_k center, and consists of a Cl_2^- molecular ion which occupies a single Cl^- site. The F center is a halide vacancy; F centers serve as electron traps. The production mechanism proposed by Pooley (43) for the paired H and F centers via the recombination of an electron with a V_k center requires that the electron be trapped by the F center.

The Cl_2^- state is frequently referred to as a "trapped-hole" colour center, as the now unbalanced charge of the Na^+ ion adjacent to the center represents a positive charge localized in a region. This unbalanced charge adds to the positive space charge in the cathode region, leading to the enhancement of the injection current, provided that a compensating negative space charge does not build up also. The effect of this space charge is to steepen the voltage gradient in the cathode region, while lowering the field in the bulk of the insulator relative to its maximum value. The effect of this electric field gradient is two-fold: first, the electrons injected into the material can now gain energy from the field in a shorter distance, and, second, V_k centers are generated in a smaller volume of the crystal. Each V_k center is a region of high potential energy; work has been done by the field to supply this energy. Thus the localization of the V_k centers by the electric field gradient implies a high energy density as well as a high space charge density in a local region. Defects may play a significant role in the trapping of charge and the localization of the centers. The possible role of defects on the formation of the initial space charge density and their subsequent effects on breakdown will be considered later.

The V_k center is a state of high potential energy with respect to the normal lattice. The source of this excess energy is the applied electric field. V_k centers are created directly from the ions of the lattice by impact ionization, and they are annihilated by electron capture, with the energy on annihilation normally going into phonon production. There is, however, another method of decay for the V_k center on capture. This mechanism, proposed by Pooley (43), involves the conversion of the V_k center into a pair of H and F centers. The H center, although chemically similar to the V_k center, cannot easily decay back to the normal lattice configuration. In order to return to the normal lattice, it is necessary for the H center to recombine with an F center.

The mechanism of Pooley requires that the F center and the H center with which it is paired be separated by several lattice spacings (at least four, and normally more), so the likelihood of H-F recombination is small. The H center retains the primary energy characteristics of the parent center. Both the V_k and the H centers represent sites at which energy is stored within the lattice, and both of these centers are the primary result of the build-up stage of breakdown.

B. Solid-Gas Reaction

1. Energetics of the Reaction

According to the proposed model, breakdown begins with the production of a high temperature, high pressure gaseous plasma within the crystal. The rate of conversion of solid to gas must be very rapid and highly exothermic if the gas is not to condense. In the present case, a reaction sequence that fulfills the requirements is

a. $(Cl_2^-)_{solid} + E3 \longrightarrow (Cl_2^{\circ})_{gas} + e^-$ $E3=1.4$ eV

b. $(Na^+)_{solid} + e^- \longrightarrow (Na^{\circ})_{gas} + E4$ $E4=5.95$eV

c. $(Na^{\circ})_{gas} + E5 \longrightarrow (Na^+)_{gas} + e^-$ $E5=5.9$ eV

The values given for the energies of the above reactions are taken from tables given in (44,45). For two atoms of Cl and two of Na to go to the gaseous state from the form of an isolated V_k (or H) center, we add equation (a) to 2 times equation (b) to equation (c), and obtain

d. $(Cl_2^-)_{solid} + 2(Na^+)_{solid} \longrightarrow (Cl_2^{\circ})_{gas} + (Na^+)_{gas} + (Na^{\circ})_{gas} + E_d$

where $E_d = 4.45$ eV is the net energy of the reaction, starting with the Cl_2^- state within the crystal. Note that reaction (d) is exothermic and does not alter the number of electrons within the system. This reaction sequence presupposes clustering of the V_k centers within a region sufficient to alter the bonding characteristics of the Na.

The reaction sequence of equation (d) could occur at any V_k (or H) center with a minute gaseous pocket being formed. This gas will be rapidly quenched unless additional conditions are met which lead to repetition of the same or similar reactions in the immediate vicinity of the first.

2. Growth of Reaction Zone

The dielectric is under high electrical stress due to the external electric field when breakdown occurs in a solid. When the gas is formed as described above, it creates a small conducting region within the dielectric. The field about the region is distorted as shown in Fig. 7.

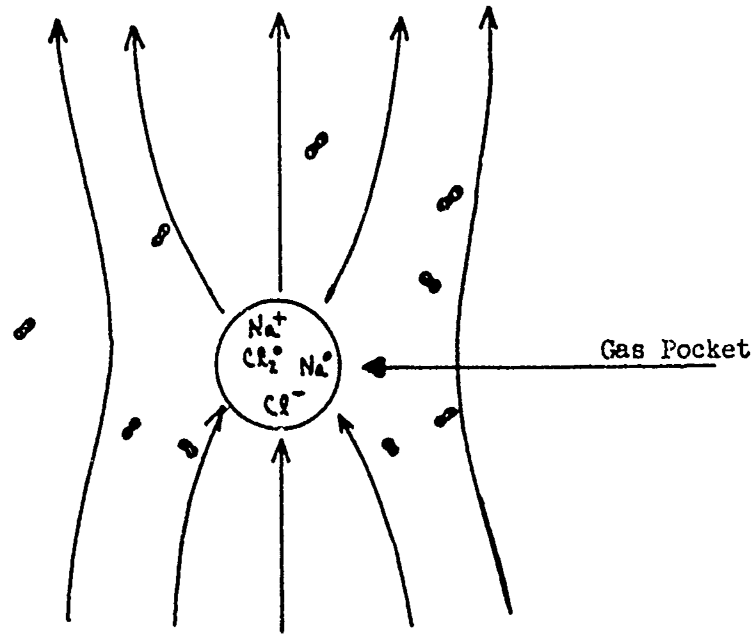
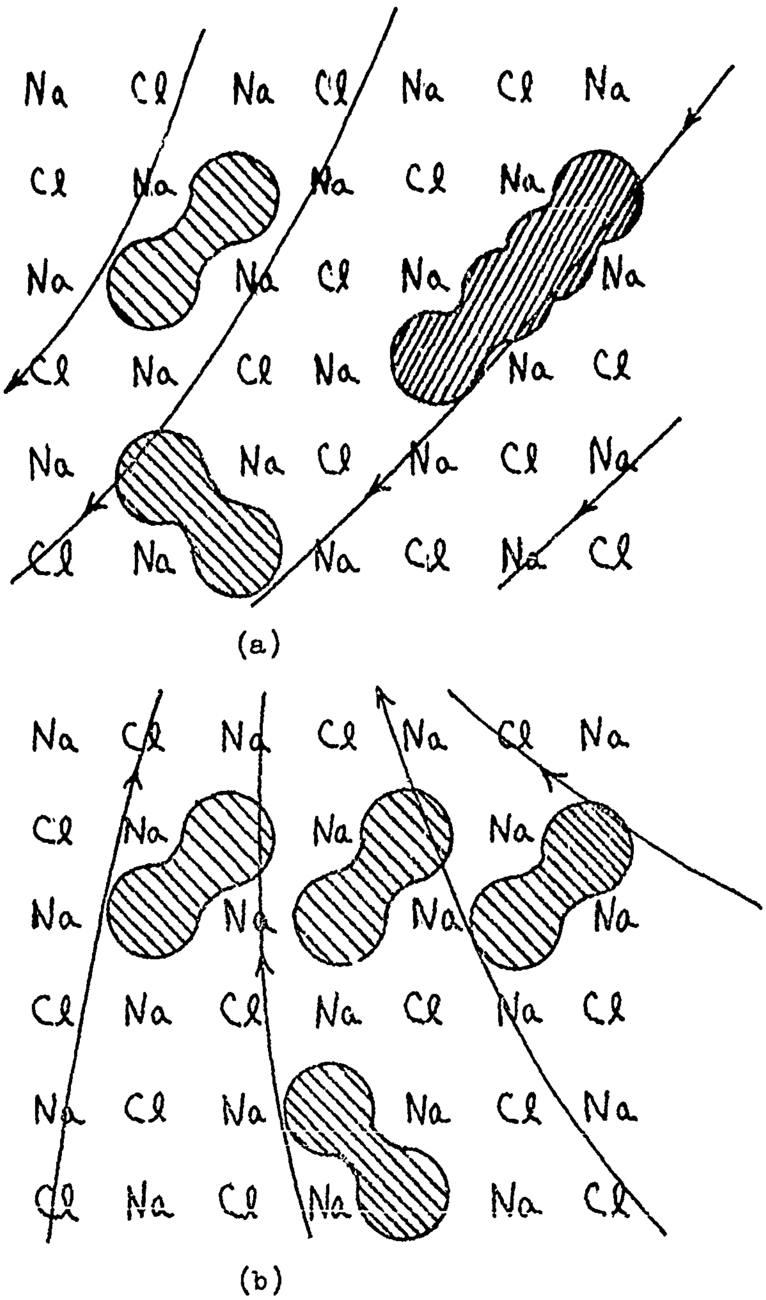


Fig. 7. Electric field distribution in the neighborhood of the internal gas pocket. Additional randomly positioned V_k centers in the vicinity of the gas pocket are also indicated. Note particularly the distortion of the field due to the gas pocket.



(a)

(b)

Fig. 8. Typical situations of V_k and H centers in an alkali halide in a non-uniform electric field region. In (a) two V_k and one H are illustrated; (b) shows four V_k centers.

Thus a field gradient exists in the region of the gas pocket, with the region of strong field being centered about the gas pocket. Such a field will exert a force on a dipole that is directed toward the region of enhanced field. Suppose that there is a distribution of H (or V_k) centers about the gaseous region. Typical situations are illustrated in Figs. 8a and 8b. The field will polarize both the Cl° and the Cl^- atoms of the V_k (or H) center. The Cl^- is electrostatically more strongly bound to the local position than the Cl° because of the surrounding Na ions. The Cl° will be polarized by the external field with a net force on it directed toward the high field region. Thus the neutral changes its affiliation to an adjacent Cl^-, that is, the V_k (or H) center moves toward the gaseous region under the action of the external field and the gradient due to the gas pocket.

The charge on a V_k center, a Cl°-Cl^- pair, can be expected to move from atom to atom of the pair. When the atom in the high field region is neutral, conditions are favorable for another jump. Thus a mechanism is available for motion of the centers toward the plasma region. The reaction of Eq. (d) can then take place and the plasma will grow in size.

3. Reactions in the Gas

In addition to the reactions of Eq.(d), further reactions can occur in the gas. These include

$$(Na^\circ)_{gas} + E1 \text{ ---------> } Na^+ + e^-$$

$$Cl_2^\circ + E2 \text{ ---------> } 2\,Cl^\circ$$

$$Cl^\circ + e^- \text{ ---------> } Cl^- + E3$$

Some of the electrons will be injected into the high field region near the gas. These can create additional V_k centers, the energy being provided by the field source.

C. Implications of the Gaseous Model

The proposed model indicates that materials with relatively large dielectric constants, and hence relatively large displacements due to polarization, should break down more easily. The reason for this is the added ionic displacement in the initial step in the formation of the V_k centers. While this will probably not be the dominant effect, as changes in the bonding structure between materials will strongly influence the breakdown, there should be a tendency among structurally similar materials toward a reduction in breakdown strength with increasing dielectric constant. Such an effect is observed experimentally (1). Polarization also contributes to the stored energy in the system, although the contribution is normally small.

The model indicates also that there should be areas in which gas production has occurred, but the gas has been quenched before completion of a channel. Such quenching could leave localized amorphous (glassy) or otherwise structurally altered regions within the dielectric. The latter could include the amorphous clusters of free metal observed in both alkali halides and other materials (23,24), and the balls of crystalline silicon produced at the edges of breakdowns in thin film SiO capacitors (12).

Neither of these points has been explained by other theories of breakdown. Additionally, the properties of the channel are substantially in agreement with the experimental evidence. Thus the existence of a hot gas within the channel will lead to electrode damage, and the light emission following breakdown would naturally be expected to be that of a gaseous plasma. The occurrence of treeing is also explicable in terms of the pressures built up in the region of the channel during the formativie stages of the channel. The production of gas in the region surrounding the channel may also aid in the formation of cracks.

The observed increase in breakdown strength with the rate of application of voltage is explained in the present model by the requirement that sufficient density of V_k centers be built up to initiate the formation of the gas.

More will be said later about the dependence of the breakdown on the presence of defects within the crystal, directional effects, ageing, and other effects.

The model presented applies directly to breakdown in ionically bonded materials. The question arises, however, concerning the applicability of the model to covalent materials. One requirement of any breakdown model is that it be relatively insensitive to bonding types within the material, as it has been shown earlier that breakdown does not depend strongly on the nature of the chemical bonds. It is thus necessary to extend our investigation to cover the case of materials which are covalently bonded, and to show that similar conditions may be expected to hold in this case also.

Cooper has recently shown that light emission occurs during the formative stage (prior to the breakdown current) in the cathode region when the material used for the dielectric was polymethylmethacrylate (PMMA) (46,47). This emission is very low in intensity and diffuse. Cooper feels it is a necessary part of the sequence of events leading to breakdown. In the above model, it is related to the process of building up sufficient energy density through formation of a space charge to make the system unstable as a solid.

In the next chapter, forming the main effort of this thesis, is a calculation to estimate quantitatively the degree of instability produced by the addition of excess charge to a molecularly bonded system. The problem has been reduced to the simplest possible case so that it could be solved without questionable compromising assumptions. By introducing great simplification, however, the problem is removed from a complex environment of the atom in a solid to that of a simple molecular cluster.

The system to be investigated is the ground state energy of the hydrogen molecular ion having two excess electrons. It is known that H_2^+ and H_2 molecules are stable in their ground state. Fischer-Hjalmars (48) has shown that the ground state of H_2^- is stable. However, no work has been done previously on the ground state energy of the doubly negative hydrogen molecular ion. By making such a calculation and comparing its results with those of the H_2 neutral and H_2^- ion, an estimate of the energy of formation of the H_2^{-2} ion and the energy release upon its dissociation can be made. These have important implications in the context of the gaseous model of breakdown.

IV. CALCULATION OF THE GROUND STATE ENERGY FOR H_2^{-2}

A. Formulation of the Problem

The ground state energy for the double negative hydrogen molecular ion is given by the solutions to the Schrödinger equation

$$H\psi = E\psi$$

where E is the energy, ψ is the wavefunction appropriate to the state, and $H = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + V$.

The wavefunction for any molecular system may be constructed from a suitable combination of atomic wavefunctions. Then the total wavefunction should correctly describe the system in the limit of large internuclear separation, which is just the case of separate atomic systems. It is desirable to choose a wavefunction that can be treated in closed form, and one that is sufficiently pliable mathematically to be solvable without requiring extraordinary mathematical procedures. The H_2^{-2} molecular ion is similar electronically to the He_2 molecule. Since Huzinga (49) has obtained the ground state wavefunction similar to his was chosen for the present calculation.

The total wavefunction is given by the Slater determinant

$$(1) \quad \psi = |\phi_g(1)\alpha(1) \quad \phi_g(2)\beta(2) \quad \phi_u(3)\alpha(3) \quad \phi_u(4)\beta(4)|$$

where $\alpha(n)$ is the spin-up and $\beta(n)$ is the spin-down spin portions of the total wavefunction for the nth electron, and the ϕ_g and ϕ_u are spatial portions of the total wavefunction, and are defined below. The use of the Slater determinant takes care of the requirements imposed on the wavefunction by the Pauli exclusion principle, and insures that the proper symmetry of the wavefunction is maintained. In this (standard) shorthand notation, the elements given are the diagonal elements of the determinant.

The space part of the wavefunction of the doubly negative hydrogen molecular ion is chosen as a superposition of two combinations of atmoic S orbitals, ϕ_g and ϕ_u. These are defined by

(2) $\phi_g = N_g(\chi_a + \chi_b)$

and

(3) $\phi_u = N_u(\chi_a' - \chi_b')$

where $\chi_a(\chi_a')$ and $\chi_b(\chi_b')$ are 1S atomic wavefunctions centered about nuclei a and b respectively. The atomic wavefunctions are defined by

(4) $\chi_a = \sqrt{\frac{\alpha^3}{\pi}}\, e^{-\alpha r_a}$ $\qquad \chi_a' = \sqrt{\frac{\gamma^3}{\pi}}\, e^{-\gamma r_a}$

and

(5) $\chi_b = \sqrt{\frac{\alpha^3}{\pi}}\, e^{-\alpha r_b}$ $\qquad \chi_b' = \sqrt{\frac{\gamma^3}{\pi}}\, e^{-\gamma r_b}$

If α and γ are different, then $\chi_a \neq \chi_a'$ and $\chi_b \neq \chi_b'$. The constants N_g and N_u are normalization constants, so that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_g{}^*\phi_g dV_a dV_b = 1 \quad \text{and} \quad \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_u{}^*\phi_u dV_a dV_b = 1$$

Then

$$(6) \quad N_g = \frac{1}{\sqrt{2}(1+S)^{\frac{1}{2}}} \quad \text{and} \quad N_u = \frac{1}{\sqrt{2}(1-T)^{\frac{1}{2}}}$$

where S and T are the overlap integrals

$$(7) \quad S = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a\chi_b dV_a dV_b \quad \text{and} \quad T = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a'\chi_b' dV_a dV_b$$

If we define $W = \alpha R$ and $x = \gamma R$, N_g and N_u may be rewritten as

$$N_g = \frac{1}{\sqrt{2}}\left[1 + e^{-w}(1 + w + \frac{w^2}{3})\right]^{-\frac{1}{2}} \quad \text{and} \quad N_u = \frac{1}{\sqrt{2}}\left[1 - e^{-x}(1 + x + \frac{x^2}{3})\right]^{-\frac{1}{2}}$$

Before proceeding further, it should be pointed out that the terms involving electron interactions with the nuclei involve the interactions of a single particle with two centers. It is natural, then, to consider carrying out the necessary calculations in a coordinate system in which there are naturally two centers present. There are two conic sections in which two focal points are present: the ellipse and the hyperbola. If we choose a coordinate system in which confocal ellipses form one coordinate, and hyperbolae, confocal to the ellipses, the other coordinate, then Fig. 9 might illustrate these coordinates.

By definition, the ellipse is that geometrical figure formed by the loci of all points having the sum of the distances from the point to two foci as a constant. Similarly, an hyperbola is the loci of

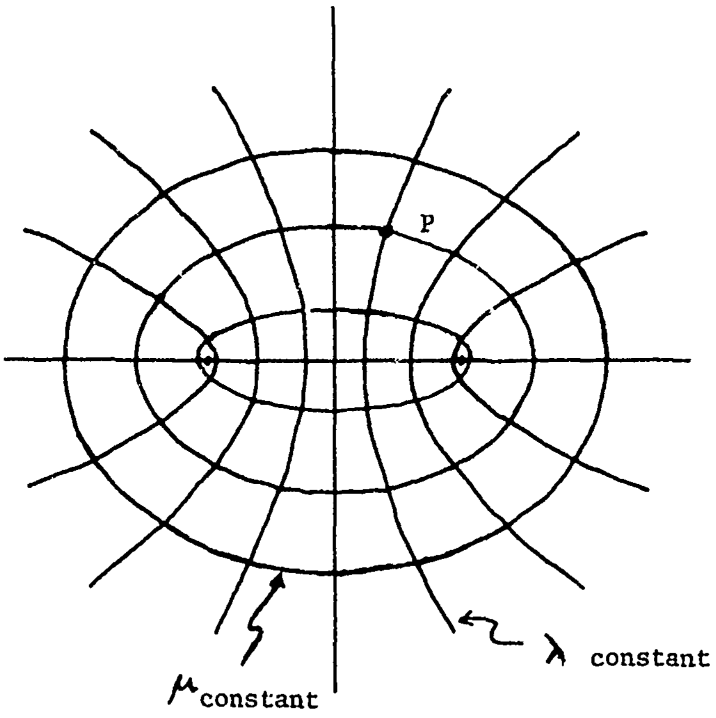


Fig. 9. Confocal coordinate system used for evaluating two-center integrals. The third coordinate is the rotation about an axis joining the two foci, which are indicated by dots in the figure.

TABLE 1

NOTATION USED FOR CONFOCAL INTEGRALS

α	screening parameter for inner electrons
γ	screening parameter for outer electrons
$\alpha(i)$	spin-up portion of the wavefunction
$\beta(i)$	spin-down portion of the wavefunction
R	internuclear separation
$w = \alpha R$	
$x = \gamma R$	
r_n	distance of electron from nth nucleus

Useful confocal coordinate relationships

$$x_{coord} = \frac{R\cos\phi}{2}\left[(\lambda^2-1)(1-\mu^2)\right]^{\frac{1}{2}}$$

$$y_{coord} = \frac{R\sin\phi}{2}\left[(\lambda^2-1)(1-\mu^2)\right]^{\frac{1}{2}}$$

x_{coord}, y_{coord}, z_{coord} are rectangular coordinates

$$z_{coord} = \frac{\lambda\mu R}{2}$$

$$\nabla^2 = \frac{4}{R^2(\lambda^2-\mu^2)}\left\{ \frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\right] + \frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}\right] + \frac{\partial}{\partial\lambda}\left[\frac{\lambda^2-\mu^2}{(\lambda^2-1)(1-\mu^2)}\frac{\partial}{\partial\mu}\right]\right\}$$

$$r_a = \frac{R(\lambda+\mu)}{2} \qquad r_b = \frac{R(\lambda-\mu)}{2}$$

all points such that the difference of the distances to the foci is a constant. In Fig. 9 this is expressed by, for point P,

$$r_a + r_b = e \qquad \text{along the ellipse}$$

$$r_a - r_b = h \qquad \text{along the hyperbola}$$

These constants are related to the coordinate system by the separation of the foci. Thus

$$\mu = \frac{r_a + r_b}{R} = \frac{e}{R} \qquad \text{and} \qquad \lambda = \frac{r_a - r_b}{R} = \frac{h}{R}$$

We also have the inverse transformation

$$r_a = (\tfrac{1}{2})\ R\ (\lambda + \mu) \qquad r_b = (\tfrac{1}{2})\ R\ (\lambda - \mu)$$

which will allow the conversion of the Hamiltonian into confocal (elliptical) coordinates. The remaining coordinate, ϕ , represents the rotation about the axis of the foci.

Before proceeding further, it is also necessary to express the Laplacian operator in confocal coordinates. In rectangular coordinates, this operator is given by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

By expressing λ, μ, and ϕ in terms of x, y, and z, and using the chain rule to obtain the necessary partial derivatives, the result may be obtained (51)

$$\nabla^2 = \frac{4}{R^2(\lambda^2-\mu^2)}\left[(\lambda^2-1)\frac{\partial^2}{\partial\lambda^2} + 2\lambda\frac{\partial}{\partial\lambda} + (1-\mu^2)\frac{\partial^2}{\partial\mu^2}\right.$$

$$\left. - 2\mu\frac{\partial}{\partial\mu} + \left(\frac{1}{\lambda^2-1} + \frac{1}{1-\mu^2}\right)\frac{\partial^2}{\partial\phi^2}\right]$$

Transformation to this coordinate system will allow the greatest simplification possible in the individual energy terms.

In calculating the energy, it is cumbersome to carry along a large number of (unit-determined) constants. Thus it is convenient to adopt the so-called atomic system of units. In this convention, masses are measured in terms of the mass of an electron, m_e, and charges in terms of the charge of a proton (equivalent in magnitude to that on an electron, but differing in sign). Angular momentum in this system is measured in units of $\hbar$. One can thus express the necessary conversion factors from this system of units to MKS units as:

$$1 \text{ at. mass unit} = m_e = 9.1 \times 10^{-31} \text{ kg}$$

$$1 \text{ at. charge unit} = e = 1.67 \times 10^{-19} \text{ Coulomb}$$

$$1 \text{ at. ang. mom. unit} = \hbar = \frac{6.67}{2\pi} \times 10^{-34} \text{ J-sec.}$$

We still have at our disposal one unit which may be arbitrarily chosen to determine all other units. (In the MKS or SI units, the meter, the kilogram, the second, and either the Coulomb or the Ampere (= Coulomb/sec) are chosen as the basic undefined units. Four units have been found sufficient to determine all other units of physical measurements.) It is convenient to consider for the last unit a length; conventionally, the length unit chosen is the radius of the innermost electron shell of hydrogen, as given by the calculation of Bohr. This unit, designated a_o, is known as a Bohr.

$$a_o = 1 \text{ Bohr} = 0.5292 \text{ Å} = 5.292 \times 10^{-11} \text{ m}.$$

As the unit of energy, two choices are frequently seen in the literature. The potential energy of a single electron attracted by a single proton (i.e., a hydrogen atom) is given by $-e^2/r$, where r is the distance between the two particles. If we take the energy at a unit distance in atomic units, we obtain

$$|-e^2/a_o| = 1 \text{ Hartree} = 1 \text{ At. energy unit.}$$

This energy is twice the energy of the hydrogen atomic ground state. Thus the energy may be related to other units by

$$1 \text{ Hartree} = 27.21 \text{ eV}.$$

The other choice of units for energy frequently made is the Rydberg, where

$$1 \text{ Rydberg} = (1/2) \text{ Hartree} = 13.605 \text{ eV}.$$

The latter unit, better adapted to calculations on hydrogen, will be used in the calculations to follow. The choice of these units will effect a great simplification in the form of the equations without any loss of physical content.

The energy of the system will be given by

$$E = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^* H \psi \, dV_1 dV_2 dV_3 dV_4 ,$$

where H is the Hamiltonian operator appropriate to the system. For the hydrogen molecular ion, H is given by

$$(8) \qquad H = -\nabla_1^2 - \nabla_2^2 - \nabla_3^2 - \nabla_4^2 - \frac{2}{r_{a1}} - \frac{2}{r_{a2}} - \frac{2}{r_{a3}} - \frac{2}{r_{a4}} - \frac{2}{r_{b1}} - \frac{2}{r_{b2}}$$

$$- \frac{2}{r_{b3}} - \frac{2}{r_{b4}} + \frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}} + \frac{2}{R}$$

where R is the internuclear separation. The R_{ij} are the distances of the ith electron from the jth electron, and r_{ai} (r_{bi}) are the distances of the ith electron from nucleus a (nucleus b). Equation (8) may be rewritten in a more compact form as

$$(8.1) \qquad H = \sum_{i=1}^{4} \left[\left(-\nabla_i^2 - \frac{2}{r_{ai}} - \frac{2}{r_{bi}} \right) + \sum_{j<i}^{4} \left(\frac{2}{r_{ij}} \right) \right] + \frac{2}{R}$$

where the sum over i is a sum over the electrons present in the system. After expanding the wavefunction, grouping, and cancelling terms which are zero (see Appendix A), the energy can be expressed in terms of the original set of basis functions as

$$(9) \qquad E = \frac{1}{4} \left\{ \int f_1^* \sum_{i=1}^{4} \left(-\nabla_i^2 - \frac{2}{r_{ai}} - \frac{2}{r_{bi}} \right) f_1 d^4V \right.$$

$$\left. + \int f_1^* \left(\sum_{i>j=1}^{4} \left(\frac{2}{r_{ij}} \right) \right) f_1 d^4V + \left(\frac{2}{R} \right) \int f_1^* f_1 d^4V \right\}$$

where

(10) $$f_1 = \phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4) - \phi_g(1)\phi_u(2)\phi_g(3)\phi_u(4)$$

$$+ \phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4) - \phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)$$

is the spatial portion of the wavefunction in terms of the original basis set, and f_1^* is the complex conjugate of f. Equation (10) may be further reduced by noting that $f_1^* = f_1$, and that

$$\int_{-\infty}^{\infty} \phi_g(1)\phi_g(1)dV_1 = \int_{-\infty}^{\infty} \phi_u(1)\phi_u(1)dV_1 = 1.$$

It is then easily seen that the terms of the energy may be written in a form analogous to that of Huzinaga (49). For ease of comparison, his notation is used here.

(11) $$E = 2H_g + 2H_u + J_{gg} + J_{uu} + 4J_{gu} - 2K_{gu} + \frac{2}{R}$$

where

(12) $$H_g = \int_{-\infty}^{\infty} \phi_g(1)(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}})\phi_g(1)dV_1$$

(13) $$H_u = \int_{-\infty}^{\infty} \phi_u(1)(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}})\phi_u(1)dV_1$$

(14) $$J_{gg} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_g(1)\phi_g(2)(\frac{2}{r_{12}})\phi_g(1)\phi_g(2)dV_1dV_2$$

(15) $$J_{uu} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_u(1)\phi_u(2)(\frac{2}{r_{12}})\phi_u(1)\phi_u(2)dV_1dV_2$$

(16) $$J_{gu} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_g(1)\phi_u(2)(\frac{2}{r_{12}})\phi_g(1)\phi_u(2)dV_1dV_2$$

(17) $$K_{gu} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_g(1)\phi_u(2)(\frac{2}{r_{12}})\phi_u(1)\phi_g(2)dV_1dV_2$$

These integrals are most conveniently handled by separating them further into the atomic wavefunctions comprising them. Note that the H_g and H_u integrals refer to interactions of the electrons with the nuclei, the J integrals (J_{gg}, J_{uu}, and J_{gu}) to interactions between "equivalent" electrons, and the K_{gu} to interactions between "unlike" electrons.

B. Evaluation of Terms

Each term may be expressed in terms of the atomic wavefunction basis set and then separated into simpler integrals over atomic states. If we consider H_g first,

(12) $$H_g = \int_{-\infty}^{\infty} \phi_g(1)(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}})\phi_g(1)dV_1$$

$$H_g = N_g^2\int_{-\infty}^{\infty}(\chi_a + \chi_b)(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}})(\chi_a + \chi_b)dV_1$$

(12.1) $$H_g = N_g^2 \{2\int_{-\infty}^{\infty}\chi_a(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}})\chi_a dV_1$$

$$+ 2\int_{-\infty}^{\infty}\chi_a(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}})\chi_b dV_1 \}$$

The first integral is

(18) $$\int_{-\infty}^{\infty}\chi_a(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}})\chi_a dV_1 = \alpha^2 - 2\alpha + \alpha\left[-\frac{2}{w} + e^{-2w}(2 + \frac{2}{w})\right]$$

and the second is

$$(19)\quad \int_{-\infty}^{\infty} \chi_a\left(-\nabla_1^2 - \frac{2}{r_{a1}} - \frac{2}{r_{b1}}\right)\chi_b dV_1 = -\alpha e^{-w}\left[(2+2w)(2-\alpha) + \left(1+w+\frac{w^2}{3}\right)\alpha\right]$$

Substitution of Eqs. (18) and (19) into Eq. (12.1) gives

$$(20)\quad H_g = 2\alpha^2 N_g^2\{\alpha - 2\left(1+\frac{1}{w}\right)(1-e^{-2w}) - e^{-w}\left[(1+w)(4-\alpha) + \frac{\alpha w^2}{3}\right]\}$$

In a like manner, H_u is evaluated as

$$(21)\quad H_u = 2\gamma^2 N_u^2\{\gamma - 2\left(1+\frac{1}{x}\right)(1-e^{-2x}) + e^{-x}\left[(1+x)(4-\gamma) + \frac{\gamma x^2}{3}\right]\}$$

The integrals involving the electron-electron interaction terms are naturally more difficult. Each will be taken in turn.

$$(14)\quad J_{gg} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_g(1)\phi_g(2)\left(\frac{2}{r_{12}}\right)\phi_g(1)\phi_g(2)dV_1dV_2$$

$$(14.1)\quad J_{gg} = N_g^4\{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_a^2(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$+ 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a(1)\chi_a^2(2)\chi_b(1)\left(\frac{2}{r_{12}}\right)dV_1dV_2 + 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\ \chi_a(2)\chi_b(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$+ 4\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a(1)\chi_a(2)\chi_b(1)\chi_b(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2 + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_b^2(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$+ 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_b^2(1)\chi_a(2)\chi_b(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2 + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(2)\chi_b^2(1)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$+ 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a(1)\chi_b(1)\chi_b^2(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2 + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_b^2(1)\chi_b^2(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2\}$$

If like terms are equated, J_{gg} becomes

$$(14.1) \qquad J_{gg} = 2N_g^4\{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_a^2(2)(\frac{2}{r_{12}})dV_1dV_2 + 4\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_a(2)\chi_b(2)$$

$$(\frac{2}{r_{12}})dV_1dV_2 + 2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a(1)\chi_b(1)\chi_a(2)\chi_b(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$+ \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_b^2(2)(\frac{2}{r_{12}})dV_1dV_2\}$$

This may be written

$$(14.2) \qquad J_{gg} = 2N_g^4\{J_{gg1} + 4J_{gg2} + 2J_{gg3} + J_{gg4}\}$$

Equation (14.2) is evaluated term-by-term as follows. The first term

$$(14.2.1) \qquad J_{gg1} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_a^2(2)(\frac{2}{r_{12}})dV_1dV_2 = \frac{5\alpha}{4}$$

Next,

$$(14.2.2) \qquad J_{gg2} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_a(2)\chi_b(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$J_{gg2} = \alpha\left[e^{-w}(2w + \frac{1}{4} + \frac{5}{8w}) - e^{-3w}(\frac{1}{4} + \frac{5}{8w})\right]$$

The third term is

$$(14.2.3) \qquad J_{gg3} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a(1)\chi_a(2)\chi_b(1)\chi_b(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$J_{gg3} = \frac{2\alpha}{5}\{- e^{-2w}(- \frac{25}{8} + \frac{23w}{4} + 3w^2 + \frac{w^3}{3}) + \frac{6}{w}\left[S^2(C+\ell n w)\right.$$

$$\left. + (S')^2 Ei(-4w) - 2SS'Ei(-2w)\right]\}$$

where

$S = e^{-w}(1 + w + \frac{w^2}{3})$

$S' = e^{+w}(1 - w + \frac{w^2}{3})$

$C = 0.57722....$ (Euler's Constant)

and $Ei(-x)$ is the exponential integral function (52). The last term is

$$(14.2.4) \qquad J_{gg4} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \chi_a^2(1)\chi_b^2(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$J_{gg4} = \alpha \left[\frac{2}{w} - e^{-2w}(\frac{2}{w} + \frac{11}{4} + \frac{3w}{2} + \frac{w^2}{3})\right]$$

In an identical manner, J_{uu} may be determined . From this point on, limits will be omitted as integrals; the limits of integration are the ranges of the variables of integration

$$(15) \qquad J_{uu} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi_u(1)\phi_u(2)(\frac{2}{r_{12}})\phi_u(1)\phi_u(2)dV_1dV_2$$

Equation (15) may be written in terms of the atomic orbitals as

$$(15.1) \qquad J_{uu} = 2N_u^4 \{\iint \chi_a'^2(2)\chi_a'^2(1)(\frac{2}{r_{12}})dV_1dV_2$$

$$- 4 \iint \chi_a'^2(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2 + 2 \iint \chi_a'(1)\chi_a'(2)\chi_b'(1)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$+ \iint \chi_a'^2(1)\chi_b'^2(2)(\frac{2}{r_{12}})dV_1dV_2\}$$

(See Appendix A for details of the expansion.)

Equation (15.1) may be written

(15.2) $J_{uu} = 2N_u^4 \{J_{uu1} - 4J_{uu2} + 2J_{uu3} + J_{uu4}\}$

where J_{uu1}, J_{uu2}, J_{uu3}, and J_{uu4} are defined and evaluated below.

(15.2.1) $J_{uu1} = \iint \chi_a'^2(1)\chi_a'^2(2)(\frac{2}{r_{12}})dV_1dV_2 = \frac{5\gamma}{4}$

(15.2.2) $J_{uu2} = \iint \chi_a'^2(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$

$$J_{uu2} = -\gamma\left[e^{-x}(2x + \frac{1}{4} + \frac{5}{8x}) - e^{-3x}(\frac{1}{4} + \frac{5}{8x})\right]$$

(15.2.3) $J_{uu3} = \iint \chi_a'(1)\chi_a'(2)\chi_b'(1)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$

$$J_{uu3} = \frac{2\gamma}{5}\{-2e^{-2x}(-\frac{25}{8} + \frac{23x}{4} + 3x^2 + \frac{x^3}{3})$$

$$+ \frac{6}{x}\; T^2(C + \ell n(x)) + (T')^2 Ei(-4x) - 2TT'Ei(-2x)\}$$

where

$T = e^{-x}(1 + x + \frac{x^2}{3})$ $\qquad$ $T' = e^{x}(1 - x + \frac{x^2}{3})$

(15.2.4) $J_{uu4} = \iint \chi_a'^2(1)\chi_b'^2(2)(\frac{2}{r_{12}})dV_1dV_2$

$$J_{uu4} = \gamma\left[\frac{2}{x} - e^{-2x}(\frac{2}{x} + \frac{11}{4} + \frac{3x}{2} + \frac{x^2}{3})\right]$$

Next, consider the first of the interaction terms between the two types of electrons, J_{gu}.

$$(16) \quad J_{gu} = \iint \phi_g(1)\phi_u(2)(\frac{2}{r_{12}})\phi_g(1)\phi_u(2)dV_1dV_2$$

$$(16.1) \quad J_{gu} = N_g^2N_u^2 \{\iint \chi_a^2(1)\chi_a'^2(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$+ \iint \chi_a(1)\chi_a'^2(2)\chi_b(1)(\frac{2}{r_{12}})dV_1dV_2 - \iint \chi_a^2(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$- \iint \chi_a(1)\chi_b(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2 + \iint \chi_b^2(1)\chi_a'^2(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$+ \iint \chi_a(1)\chi_b(1)\chi_a'^2(2)(\frac{2}{r_{12}})dV_1dV_2 - \iint \chi_a(1)\chi_b(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$- \iint \chi_b^2(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2 - \iint \chi_a^2(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$- \iint \chi_a(1)\chi_b(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2 + \iint \chi_a^2(1)\chi_b'^2(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$+ \iint \chi_a(1)\chi_b(1)\chi_b'^2(2)(\frac{2}{r_{12}})dV_1dV_2\}$$

If J_{gu} in Eq. (16.1) is expanded in terms of the basis set, J_{gu} may be written

$$(16.2) \quad J_{gu} = 2N_g^2N_u^2 \{\iint \chi_a^2(1)\chi_a'^2(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$+ \iint \chi_a^2(1)\chi_b'^2(2)(\frac{2}{r_{12}})dV_1dV_2 - 2\iint \chi_a(1)\chi_b(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$- 2\left[\iint \chi_a^2(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2 - \iint \chi_a'^2(2)\chi_a(1)\chi_b(2)(\frac{2}{r_{12}})dV_1dV_2\right]\}$$

Then, using a symbol to represent each integral, J_{gu} may be written

$$(16.3) \qquad J_{gu} = 2N_g^2 N_u^2 \{J_{gu1} + J_{gu2} - 2J_{gu3} - 2[J_{gu4} - J_{gu5}]\}$$

These terms are defined and evaluated below.

$$(16.3.1) \qquad J_{gu1} = \iint \chi_a^2(1)\chi_a'^2(2)(\frac{2}{r_{12}})dV_1dV_2 = 2\gamma\left[1 - \frac{\gamma^2}{(\alpha+\gamma)^2} - \frac{\alpha\gamma^2}{2(\alpha+\gamma)^3}\right]$$

$$(16.3.2) \qquad J_{gu2} = \iint \chi_a^2(1)\chi_b'^2(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$J_{gu2} = \frac{\gamma^3}{R}\{(1 - e^{-2x})(\frac{1+x}{\gamma^3}) - \frac{1}{\gamma^3}\left[(x - 1) + e^{-2x}(x + 1)\right]$$

$$- \frac{(e^{-2x} - e^{-2w})(1 + w + x)}{(\alpha - \gamma)(\alpha + \gamma)^2} + \frac{e^{-2x}(1 - w + x) - e^{-2w}(1 + w - x)}{(\alpha + \gamma)(\alpha - \gamma)^2}$$

$$- \frac{\alpha\left[e^{-2x} - e^{-2w}\right](1 + w + x)}{(\alpha - \gamma)(\alpha + \gamma)^2}$$

$$+ \frac{\alpha}{(\alpha+\gamma)(\alpha-\gamma)^3}\left[e^{-2x}(1-w+x) + \frac{e^{-2x}(\alpha-\gamma)^2R^2}{2} - e^{-2w}(1+w-x+\frac{(\alpha-\gamma)^2R^2}{2})\right]\}$$

$$(16.3.3) \qquad J_{gu3} = \iint \chi_a(1)\chi_b(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1dV_2$$

$$J_{gu3} = \frac{2\gamma^3}{5}\{\frac{-6w(1+w+x+\frac{(\alpha+\gamma)^2R^2}{3})e^{-w-x}}{(\alpha + \gamma)^3R} - 5\left[\frac{e^{-x}(1+x)}{\gamma^2}\right]$$

$$+ \frac{e^{-w-x}(1+w+x)}{(\alpha+\gamma)^2} + \frac{we^{-w-x}(1+w+x+\frac{2(\alpha+\gamma)^2R^2}{3})}{(\alpha+\gamma)^3R} - \frac{6S'TE\ell(-2w)}{\gamma^2x}$$

$$+ \frac{6S'T'E\ell(-2(w+x))}{\gamma^2x} - \left[\frac{(6S'e^{-2w-x})}{\gamma^2x}\right]\left[\frac{\gamma^2(1+2w+2x)}{2(\alpha+\gamma)^2} + \frac{(1-x)}{\alpha+\gamma}\right]$$

$$+ \frac{6Se^{-x}}{\gamma^2 x}\left[\frac{\gamma^2}{2(\alpha+\gamma)^2} + \frac{\gamma(1+x)}{\alpha+\gamma}\right] + \frac{6S}{\gamma^2 x}\left[T\ell n(2) - T'Ei(-2x) - xe^{-x}\right]$$

$$+ \frac{6ST}{\gamma^2 x}\left[\ell n(w) - \ell n(1 + \frac{\alpha}{\gamma}) + C\right]\}$$

$$(16.3.4) \qquad J_{gu4} = \iint \chi_a^2(1)\chi_a'(2)\chi_b'(2)(\frac{2}{r_{12}})dV_1 dV_2$$

$$J_{gu4} = \frac{\gamma^3}{R}\{ \frac{2e^{-x}(1+x)R}{\gamma^2} - (e^{-x} - e^{-2w-x})(\frac{1+w+x}{\alpha(\alpha+\gamma)^2})$$

$$- \frac{e^{-2w-x}(w+1) + e^{-x}(w-1)}{\alpha^2(\alpha+\gamma)} - \frac{(e^{-x} - e^{-2w-x})(1+w+x+\frac{(\alpha+\gamma)^2R^2}{2})}{(\alpha+\gamma)^3}$$

$$+ \frac{e^{-x}(2-2w+w^2) - e^{-2w-x}(2+2w+w^2)}{2\alpha^2(\alpha+\gamma)}\}$$

$$(16.3.5) \qquad J_{gu5} = \iint \chi_a'^2(2)\chi_a(1)\chi_b(1)(\frac{2}{r_{12}})dV_1 dV_2$$

$$J_{gu5} = \frac{\alpha^3}{R}\{ \frac{2e^{-w}(1+w)R}{\alpha^2} - \frac{(e^{-w} - e^{-2x-w})(1+w+x)}{\gamma(\alpha+\gamma)^2}$$

$$- \frac{e^{-2x-w}(1+x) + e^{-w}(x-1)}{\gamma^2(\alpha+\gamma)} - \frac{(e^{-w} - e^{-2x-w})(1+w+x+\frac{(\alpha+\gamma)^2R^2}{3})}{(\alpha+\gamma)^3}$$

$$+ \frac{e^{-w}(2-2x+x^2) - e^{-2x-w}(2+2x+x^2)}{2\gamma^2(\alpha+\gamma)}\}$$

The final set of interaction terms which must be considered are in the K_{gu} term: it is the most troublesome of all the terms in the evaluation of the energy.

$$(17) \quad K_{gu} = \iint \phi_g(1)\phi_u(2)\left(\frac{2}{r_{12}}\right)\phi_u(1)\phi_g(2)\,dV_1dV_2$$

It is easy to see why this integral is difficult; it involves the interchange of an electron in one orbital with that in another orbital. The expansion of K_{gu} in terms of the basis set is

$$(17.1) \quad K_{gu} = 2N_g^2N_u^2 \{\iint \chi_a(1)\chi_a'(1)\chi_a(2)\chi_a'(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$- \iint \chi_a(1)\chi_b'(1)\chi_a'(2)\chi_b(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2 - 2\iint \chi_a(1)\chi_a'(1)\chi_a(2)\chi_b'(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$- \iint \chi_a(1)\chi_a'(1)\chi_b(2)\chi_b'(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2 + \iint \chi_a(1)\chi_b'(1)\chi_a(2)\chi_b'(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$+ 2\iint \chi_a(1)\chi_a'(1)\chi_a'(2)\chi_b(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2\}$$

Equation (17.1) can be expressed as

$$(17.2) \quad K_{gu} = 2N_g^2N_u^2 \{K_{gu1} - K_{gu2} - 2[K_{gu3} - K_{gu4}] - K_{gu5}\}$$

where

$$(17.3.1) \quad K_{gu1} = \iint \chi_a(1)\chi_a'(1)\chi_a(2)\chi_a'(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$(17.3.2) \quad K_{gu2} = \iint \chi_a(1)\chi_a'(1)\chi_b(2)\chi_b'(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$(17.3.3) \quad K_{gu3} = \iint \chi_a(1)\chi_a'(1)\chi_a(2)\chi_b'(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

$$(17.3.4) \quad K_{gu4} = \iint \chi_a(1)\chi_a'(1)\chi_a'(2)\chi_b(2)\left(\frac{2}{r_{12}}\right)dV_1dV_2$$

(17.3.5) $$K_{gu5} = \iint \chi_a(1)\chi_b'(1)\chi_a(2)\chi_b'(2)\left(\frac{2}{r_{12}}\right)dV_1 dV_2$$

$$- \iint \chi_a'(1)\chi_b(1)\chi_a'(2)\chi_b(2)\left(\frac{2}{r_{12}}\right)dV_1 dV_2$$

The term K_{gu5} will have to be handled separately—it is the only one of the integrals involved which cannot be solved in closed form. (However difficult the other integrals may appear, they each possess "closed" form solutions in terms (at worst) of transcendental functions.) The values of the other terms are:

(17.3.1.1) $$K_{gu1} = \frac{40\alpha^3\gamma^3}{(\alpha+\gamma)^5}$$

(17.3.2.1) $$K_{gu2} = \frac{8\alpha^3\gamma^3}{(\alpha+\gamma)^6 R}\{16-e^{-w-x}\left[16+11(w+x)+3(\alpha+\gamma)^2R^2+\frac{(\alpha+\gamma)^3R^3}{3}\right]\}$$

(17.3.3.1) $$K_{gu3} = \frac{8\alpha^3\gamma^3}{(\alpha+\gamma)^3}\{\frac{8\left[e^{-x}(-2\gamma+(\alpha^2-\gamma^2)R) + 2\gamma e^{-w}\right]}{(\alpha^2 - \gamma^2)^2 R}$$

$$- \frac{(e^{-x} - e^{-2w-x})}{\alpha(\alpha + \gamma)^2}\left(\frac{3}{2} + \frac{3}{2}(w+x) + \frac{(\alpha+\gamma)^2R^2}{4}\right)$$

$$- \frac{e^{-2w-x}(w+1) + e^{-x}(w-1)}{\alpha^2(\alpha + \gamma)R} + \frac{e^{-x}(w^2-2w+2) - e^{-2w-x}(w^2+2w+2)}{4\alpha^3 R}\}$$

(17.3.4.1) $$K_{gu4} = \frac{8\alpha^3\gamma^3}{(\alpha+\gamma)^3}\{\frac{8e^{-w}(-2\alpha+(\gamma^2-\alpha^2)R) + 16\ e^{-x}}{(\gamma^2 - \alpha^2)^2 R}$$

$$- \frac{(e^{-w} - e^{-w-2x})}{\gamma(\alpha + \gamma)^2}\left(\frac{3}{2} + \frac{3}{2}(w+x) + \frac{(\alpha+\gamma)^2}{4}R^2\right)$$

$$- \frac{e^{-w-2x}(x+1) + e^{-w}(x-1)}{\gamma^{2}(\alpha + \gamma)R} + \frac{e^{-w}(x^{2}-2x+2) - e^{-w-2x}(x^{2}+2x+2)}{4\gamma^{3}R}$$

The remaining integrals (designated as K_{gu5}) are best handled by returning to a combined form, so that the integrand will possess symmetry properties making the solution a bit easier to obtain. In this form,

$$(17.3.5.1) \quad K_{gu5} = \iint (\chi_a(1)\chi_b'(1)(\frac{2}{r_{12}}))(\chi_a(2)\chi_b'(2) - \chi_a'(2)\chi_b(2))dV_1dV_2$$

The evaluation of this integral will be treated in detail, as this integral presents the greatest difficulty of those encountered.

Consider first the integral over the separation, namely

$$(22) \quad I_{K1} = \int \chi_a(1)\chi_b'(1)(\frac{2}{r_{12}})dV_1$$

As the integral I_{K1} (Eq. (22)) involves $(\frac{1}{r_{12}})$, where r_{12} is the separation of the two electrons, it is necessary to express $(\frac{1}{r_{12}})$ in terms of confocal (elliptic) coordinates. This expansion, normally termed the Neumann expansion, is

$$(23) \quad (\frac{1}{r_{12}}) = \frac{2}{R} \sum_{k=o}^{\infty} \sum_{m=-k}^{k} (-1)^{m}(2k+1) \left[\frac{(k-|m|)!}{(k+|m|)!}\right]^{2}$$

$$\times \quad P_k^{|m|}\left[\lambda(a)\right]Q_k^{|m|}\left[\lambda(b)\right]P_k^{|m|}(\mu_1)P_k^{|m|}(\mu_2)e^{im(\phi_1-\phi_2)}$$

where $(\lambda_i, \mu_i, \phi_i)$ are the coordinates of the ith electron, and $[\lambda(a)]$ is the lesser and $[\lambda(b)]$ the greater of λ_1 and λ_2. The $P_k^{|m|}$

and $Q_k^{|m|}$ are the associated Legendre functions of the first and second kinds, respectively (60).

The integral of Eq. (22) over ϕ_1 and ϕ_2 may be carried out immediately by noting that

$$\int_0^{2\pi} d\phi_1 \int_0^{2\pi} \phi \left[\sum_{k=0}^{\infty} \sum_{m=-k}^{k} e^{im(\phi_1-\phi_2)} \right] d\phi_1 d\phi_2 = 0, \quad m \neq 0$$

since

$$\int_0^{2\pi} e^{-im\phi} d\phi = \frac{1}{im} \left[e^{im\phi} \right]_0^{2\pi} = \frac{1}{im} [1-1] = 0$$

Thus ϕ becomes a nugatory coordinate, and m is zero for a non-vanishing integral. For m = 0,

$$\int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 f(\lambda_1, \lambda_2, \mu_1, \mu_2) = 4\pi^2 f(\lambda_1, \lambda_2, \mu_1, \mu_2)$$

Since m = 0, there is no azimuthal dependence, so the separation between the two electrons can be expanded using the expansion

$$\chi_a(1)\chi_b'(1) = \frac{\sqrt{\alpha^3\gamma^3}}{\pi} e^{-(\alpha+\gamma)R\lambda/2} e^{-(\alpha-\gamma)R\mu/2}$$

The integral of Eq. (22) can be written

$$(22.1) \quad I_{k1} = \left(\frac{\sqrt{\alpha^3\gamma^3}}{\pi}\right)\left(\frac{R^3}{8}\right)(2\pi)\left(\frac{4}{R}\right) \sum_{k=0}^{\infty} (2k+1) \int_{-1}^{1}\int_{1}^{\infty} (\lambda^2-\mu^2) P_k[\lambda(a)]$$

$$\times \quad Q_k[\lambda(b)] P_k(\mu_1) P_k(\mu_2) e^{-(\alpha+\gamma)R\lambda_1/2} e^{-(\alpha-\gamma)R\mu_1/2} d\lambda_1 d\mu_1$$

in confocal coordinates, where the integration over azimuthal dependence has already been carried out. This may be rewritten as

$$(22.2) \qquad I_{K1} = \sqrt{\alpha^3\gamma^3}\, R^2 \sum_{k=0}^{\infty} (2k+1) \int_{-1}^{1}\int_{1}^{\infty} (\lambda^2-\mu^2) P_k\left[\lambda(a)\right] Q_k\left[\lambda(b)\right]$$

$$\times \quad P_k(\mu_1)P_k(\mu_2)e^{-(\alpha+\gamma)R\lambda_1/2}\, e^{-(\alpha-\gamma)R\mu_1/2}\, d\lambda_1 d\mu_1$$

It is the presence of the exponential factor $e^{\frac{-(\alpha-\gamma)R\mu_1}{2}}$ which makes this integral difficult: this factor prevents simplification by use of orthogonality conditions of the Legendre functions.

To proceed further, make the expansion

$$(24) \qquad e^{-(\alpha-\gamma)R\mu/2} = \sum_{j=0}^{\infty} \left(-(\alpha-\gamma)\frac{R\mu}{2}\right)^j \left(\frac{1}{j!}\right) = \sum_{j=0}^{\infty} \left(\left[-\frac{(\alpha-\gamma)R}{2}\right]^j \frac{\mu^j}{j!}\right)$$

The μ^j, however, may easily be replaced in this series by Legendre polynomials, which will be truncated after only a few terms. This allows the use of the orthogonality properties of the Legendre polynomials.

It will be noted at this point that a "straightforward" expansion in orthonormal functions (i.e., in Legendre polynomials) could have been used in preference to the treatment adopted. The drawback to this procedure lies in the problem of representing the exponential adequately with only a few terms; approximately four times the number of terms would have been required for acceptable accuracy with the "straightforward" approach as were actually used with the approach given here.

The original series will thus be replaced by the new series

$$e^{-(\alpha-\gamma)r\mu/2} \approx \sum_{j=0} A_j P_j(\mu)$$

where the coefficients A_j will be evaluated by direct comparison of the power series expansion with the expansion in Legendre polynomials when the power series is expanded in terms of Legendre polynomials.

Substitution of the expansion of Eq. (24) into the integral gives

$$(22.3) \quad I_{K1} = \sqrt{\alpha^3\gamma^3}\, R^3 \sum_{k=0}^{\infty} (2k+1) \int_{-1}^{1}\int_{1}^{\infty} (\lambda_1^2-\mu_1^2) P_k[\lambda(a)]\, Q_k[\lambda(b)]$$

$$\times \quad P_k(\mu_1) P_k(\mu_2)\, e^{-(\alpha+\gamma)R\mu_1/2} \sum_{j=0} A_j P_j(\mu_1)\, d\lambda_1 d\mu_1$$

The u_1 dependence of $(\lambda_1^2-\mu_1^2)$ involves only $P_0(\mu_1)$ and $P_2(\mu_1)$. Hence, the integrand will be expanded to obtain the $P_k(\mu)$ dependence. Then the summation over k involves only a finite number of terms. Thus, the expansion of $(\lambda_1^2-\mu_1^2)$ is

$$(25) \quad (\lambda_1^2 - \mu_1^2) = (\lambda_1^2 - \tfrac{1}{3})P_0(\mu_1) - \tfrac{2}{3} P_2(\mu_1)$$

$$(26) \quad (\lambda_1^2 - \mu_1^2) \sum_{j=0} A_j P_j(\mu_1) = A_0(\lambda^2 - \tfrac{1}{3})P_0(\mu_1) - \frac{2A_0}{3} P_2(\mu_1)$$

$$+ A_1(\lambda_1^2 - \tfrac{1}{3})P_1(\mu_1) - \frac{2A_1}{3} P_2(\mu_1)P_1(\mu_1) + A_2(\lambda_1^2 - \tfrac{1}{3})P_2(\mu_1)$$

TABLE 2

FIRST FEW LEGENDRE POLYNOMIALS

n	$P_n(x)$
1	x
2	$(\frac{1}{2})(3x^2 - 1)$
3	$(\frac{1}{2})(5x^3 - 3x)$
4	$(\frac{1}{8})(35x^4 - 30x^2 + 3)$
5	$(\frac{1}{8})(63x^5 - 70x^3 + 15x)$

n	$Q_n(x)$
0	$(\frac{1}{2})\ell n(\frac{x + 1}{x - 1})$
1	$(\frac{1}{2})x\ell n(\frac{x + 1}{x - 1}) - 1$
2	$(\frac{1}{4})(3x^2 - 1)\ell n(\frac{x + 1}{x - 1}) - (\frac{3}{2})x$
3	$(\frac{1}{4})(5x^3 - 3x)\ell n(\frac{x + 1}{x - 1}) - (\frac{5}{2})x^2 + (\frac{2}{3})$
4	$(\frac{1}{16})(35x^4 - 30x^2 + 3)\ell n(\frac{x + 1}{x - 1}) - (\frac{35}{8})x^3 + (\frac{55}{24})x$
5	$(\frac{1}{16})(63x^5 - 70x^3 + 15x)\ell n(\frac{x + 1}{x - 1}) - (\frac{63}{8})x^4 + (\frac{49}{8})x^2 - \frac{8}{15}$

$$-\frac{2A_2}{3} P_2(\mu_1)P_2(\mu_1) + \ldots.$$

$$= \sum_j A_j \left(\lambda_1^2 - \frac{1}{3}\right)P_j(\mu_1) - \frac{2}{3} \sum_j A_j P_j(\mu_1)P_2(\mu_1)$$

(For convenience, Table 2 contains the first few Legendre polynomials.)

Next, the products of $P_j(\mu)P_2(\mu)$ are expanded and the series truncated for j = 3.

$$P_1(\mu_1)P_2(\mu_1) = \frac{3}{5} P_3(\mu_1) + \frac{2}{5} P_1(\mu_1)$$

$$P_2(\mu_1)P_2(\mu_1) = \left(\frac{18}{35}\right) P_4(\mu_1) + \frac{2}{7} P_2(\mu_1) + \frac{1}{5} P_0(\mu_1)$$

$$P_3(\mu_1)P_2(\mu_1) = \frac{1}{63} \left[30\, P_5(\mu_1) + \frac{84}{5} P_3(\mu_1) + \frac{187}{10} P_1(\mu_1)\right]$$

These results reduce the integral of Eq. (22.3) to the form

$$(22.4) \qquad I_{K1} = \sqrt{\alpha^3\gamma^3}\, R^3 \sum_{K=0}^{\infty} (2k+1) \int_{-1}^{1}\int_{1}^{\infty} P_k[\lambda(a)]\, Q_k[\lambda(b)]\, P_k(\mu_2)$$

$$X \quad e^{-(\alpha+\gamma)R\lambda_1/2}\, P_k(\mu_2) \left[\left(\lambda_1^2 - \frac{1}{3}\right) \sum_{j=0} A_j P_j(\mu_1) - \frac{2}{3} \sum_j B_j P_j(\mu_1)\right] d\lambda_1 d\mu_1$$

where the coefficients B_j are obtained by a direct summation of the coefficients of $P_j(\mu_1)$ in the expansion. The orthogonality of the Legendre polynomials is expressed by the equation

$$(27) \qquad \int_{-1}^{1} P_k(z)P_\ell(z)dz = \left(\frac{2}{2\ell+1}\right) \delta_{k\ell}$$

This allows Eq. (22.4) to be written

$$(22.5) \qquad I_{K1} = \sqrt{\alpha^3\gamma^3}\, R^2 \{ \sum_{k,\ell} (2k+1)\left(\frac{2}{2\ell+1}\right) \delta_{k\ell}$$

$$X \int_1^\infty P_k[\lambda(a)]\, Q_k[\lambda(b)]\, P_k(\mu_2)\, e^{-(\alpha+\gamma)R\mu_1/2} \left[(\lambda_1^2 - \frac{1}{3})A_\ell - \frac{2B_\ell}{3}\right] d\lambda_1$$

Due to the involved nature of the integrals in the series expansion, it was found necessary to truncate the series after three terms. The entire K_{gu} contribution to the total energy amounts to only about five percent of the total energy (the term is positive, and thus is a weakening of the bonding), so that its truncation did not lead to a significant error in the total energy. For an internuclear separation of one Bohr, this truncation resulted in an error of about eight percent in the value of the K_{gu} term, as compared with the results given for a similar term by Huzinaga (51) (see Appendix F for the numerical values in the comparison). This accuracy was felt to be sufficient, as the addition of a further term to the series would have greatly lengthened the calculation and required an unreasonably long delay in the completion of the work.

At this point, it is convenient to give the coefficients resulting from the expansion of the exponential and the product of this expansion with the $(\lambda_1^2-\mu_1^2)$ term. Coefficients are given in Table 3 for an expansion of the exponential through the fifth power. Only the terms with $j<3$ were used in the calculations.

After the integration over μ_1,

$$(22.6) \qquad I_{k1} = 2\sqrt{\alpha^3\gamma^3}\, R^2 \sum_k \{A_k \int_1^\infty P_k[\lambda(a)]\, Q_k[\lambda(b)]\, P_k(\mu_2)$$

$$\times \quad e^{-(\alpha+\gamma)R\lambda_1/2}(\lambda_1^2 - \tfrac{1}{3})d\lambda_1 - B_k \int_1^\infty P_k[\lambda(a)]Q_k[\lambda(b)]P_k(\mu_2)$$

$$\times \quad e^{-(\alpha+\gamma)R\lambda_1/2}d\lambda_1\}$$

In Eq. (22.6), $\lambda(a)$ is the lesser and $\lambda(b)$ the greater of λ_1, λ_2. Thus the integration over λ_1 involves integration over the $P_k[\lambda(a)]$ for values of λ_1 less than λ_2, with $Q_k(\lambda_2)$ independent of λ_1, and integration over $Q_k[\lambda(b)]$ for values of λ_1 greater than λ_2, with $P_k(\lambda_2)$ constant. It is therefore necessary to take the integral separately over the range $\lambda_1 < \lambda_2$ and $\lambda_1 > \lambda_2$.

Equation (22.6) will be expanded term by term. Let $m = (\alpha+\gamma)R$ for convenience. Let us consider first the k=0 term:

$$(28) \qquad I_{28} = \int_1^\infty P_0[\lambda(a)]Q_0[\lambda(b)]P_0(\mu_2)e^{-(\alpha+\gamma)R\lambda_1/2}(\lambda_1^2 - \tfrac{1}{3})d\lambda_1$$

$$= P_0(\mu) \;\{Q_0(\mu_2) \int_1^{\lambda_2} e^{-m\lambda_1/2}(\lambda_1^2 - \tfrac{1}{3})d\lambda_1 + \int_\lambda^\infty (\tfrac{1}{2})\ell n(\frac{\lambda_1+1}{\lambda_1-1})$$

$$\times \quad e^{-m\lambda_1/2}(\lambda_1^2 - \tfrac{1}{3})d\lambda_1\}$$

The first of these is evaluated in Table B-1 of Appendix B. The second integral does not contain the value $\lambda_1=1$, so there are no singularities to be avoided.

Using the values tabulated in Table 4, the integral of Eq. (28) may be written

$$(28.1) \qquad I_{28} = P_o(\mu) \;\{\tfrac{1}{2}\ell n(\frac{\lambda+1}{\lambda-1}) \left[\frac{2e^{-m/2}}{(m/2)^3} \;(1+\frac{m\lambda}{2}+\frac{m^2}{8}(\lambda^2 - \tfrac{1}{3}))\right]_1^{\lambda_2}$$

$$+ \frac{1}{2} \left[\frac{16}{m^3} \left[(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8})e^{-m\lambda/2}\ell n(\frac{\lambda+1}{\lambda-1}) - (1 - \frac{m}{2} + \frac{m^2}{8})e^{m/2}Ei(- \frac{m}{2}(\lambda+1))\right.\right.$$

$$\left.+ (1 + \frac{m}{2} + \frac{m^2}{8})e^{-m/2}Ei(- \frac{m}{2}(\lambda-1)) - \frac{m}{2} e^{-m\lambda/2}\right] - \frac{2}{3m} \left[e^{-m\lambda/2}Ei(\frac{\lambda+1}{\lambda-1})\right.$$

$$\left.\left.- e^{m/2}Ei(- \frac{m}{2}(\lambda+1)) + e^{-m/2}Ei(- \frac{m}{2}(\lambda-1))\right] \right]\}$$

Equation (28.1) may be rearranged as

$$(28.2) \qquad I_{28} = \frac{4}{m^3} \{\frac{1}{2}\ell n(\frac{\lambda+1}{\lambda-1}) \left[e^{-m/2}(\frac{m^2}{6}+m+2)\right] - e^{m/2}(1-\frac{m}{2}+\frac{m^2}{12})Ei(-\frac{m}{2}(\lambda+1))$$

$$+ e^{-m/2}(1 + \frac{m}{2} + \frac{m^2}{12})Ei(- \frac{m}{2}(\lambda-1)) - e^{-m\lambda/2}(\frac{m}{2})\}$$

The comparable B term for k=0 is

$$(29) \qquad I_{29} = P_0(\mu_2) \int_1^\infty P_0[\lambda(a)]Q_o[\lambda(b)]e^{-m\lambda/2}d\lambda$$

$$= \frac{P_0(\mu_2)}{m} \{e^{-m\lambda/2}\ell n(\frac{\lambda+1}{\lambda-1}) - e^{-m/2}Ei(- \frac{m}{2}(\lambda+1)) + e^{m/2}Ei(- \frac{m}{2}(\lambda-1))\}$$

The A_1 term of Eq. (22.5) is

$$(30) \qquad I_{30} = \int_1^\infty P_1[\lambda(a)]Q_1[\lambda(b)]P_1(\mu_2)e^{-m\lambda_1/2}(\lambda_1^2 - \frac{1}{3})d\lambda_1$$

$$= P_1(\mu_2) \{Q_1(\lambda_2) \int_1^{\lambda_2}\lambda_1 e^{-m\lambda_1/2}(\lambda_1^2 - \frac{1}{3})d\lambda_1 - \lambda_2 \int_{\lambda_2}^\infty e^{-m\lambda_1/2}(\lambda_1^2 - \frac{1}{3})d\lambda_1$$

$$+ \frac{\lambda_2}{2} \int_{\lambda_2}^\infty \lambda_1\ell n(\frac{\lambda_1+1}{\lambda_1-1}) (\lambda_1^2 - \frac{1}{3})e^{-m\lambda_1/2}d\lambda_1\}$$

TABLE 3

EXPANSION COEFFICIENTS

j	A_j	B_j
0	$1 - \frac{(\alpha-\gamma)^2R^2}{24} + \frac{(\alpha-\gamma)^4R^4}{1940}$	$\frac{2A_2}{15}$
1	$-\frac{(\alpha-\gamma)R}{2} - \frac{(\alpha-\gamma)^3R^3}{80} - \frac{(\alpha-\gamma)^5R^5}{63(3840)}$	$\frac{187A_3}{15} + \frac{4A_1}{15}$
2	$\frac{(\alpha-\gamma)^2R^2}{12} + \frac{(\alpha-\gamma)^4R^4}{679}$	$\frac{4A_4}{21} + \frac{4A_2}{21} + \frac{2A_0}{3}$
3	$-\frac{(\alpha-\gamma)^3R^3}{120} - \frac{(\alpha-\gamma)^5R^5}{5040}$	$\frac{130A_5}{99} + \frac{56A_3}{5} + \frac{2A_1}{5}$
4	$\frac{2(\alpha-\gamma)^4R^4}{3395}$	$\frac{40A_4}{231} + \frac{12A_2}{35}$
5	$-\frac{(\alpha-\gamma)^5R^5}{30240}$	$\frac{20A_4}{117} + \frac{20A_3}{63}$
6	0	$\frac{10A_4}{33}$
7	0	$\frac{42A_5}{143}$

TABLE 4

INTEGRALS ENCOUNTERED IN EXPANDING UNLIKE ELECTRON INTERACTION TERM K_{gu}

$$\int_1^\lambda e^{-my/2}\, y^n dy \;=\; (Dn) - (Dn\lambda)$$

n	(Dn) - (Dnλ)
0	$\frac{2}{m}\left[e^{-m/2} - e^{-m\lambda/2}\right]$
1	$\frac{4}{m^2}\left[e^{-m/2}(1 + \frac{m}{2}) - e^{-m\lambda/2}(1 + \frac{m\lambda}{2})\right]$
2	$\frac{16}{m^3}\left[e^{-m/2}(1 + \frac{m}{2} + \frac{m^2}{8}) - e^{-m\lambda/2}(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8})\right]$
3	$\frac{96}{m^4}\left[e^{-m/2}(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}) - e^{-m\lambda/2}(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8} + \frac{m^3\lambda^3}{48})\right]$
4	$\frac{24(32)}{m^5}\left[e^{-m/2}(1+\frac{m}{2}+\frac{m^2}{8}+\frac{m^3}{48}+\frac{m^4}{384}) - e^{-m\lambda/2}(1+\frac{m\lambda}{2}+\frac{m^2\lambda^2}{8}+\frac{m^3\lambda^3}{48}+\frac{m^4\lambda^4}{384})\right]$
5	$\frac{120(64)}{m^6}\left[e^{-m/2}(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48} + \frac{m^4}{384} + \frac{m^5}{3840}) - e^{-m\lambda/2}\right.$ $\left.(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8} + \frac{m^3\lambda^3}{48} + \frac{m^4\lambda^4}{384} + \frac{m^5\lambda^5}{3840})\right]$

n	$C_n = \int_1^\infty d^{-my}\, y^n dy$

0	$e^{-m}(\frac{1}{m})$
1	$\frac{e^{-m}}{m^2}(1 + m)$
2	$\frac{e^{-m}}{m^3}(2 + 2m + m^2)$
3	$\frac{e^{-m}}{e^4}(6 + 6m + 3m^2 + m^3)$
4	$\frac{e^{-m}}{e^5}(m^4 + 4m^3 + 12m^2 + 24m + 24)$
5	$\frac{e^{-m}}{m^6}(m^5 + 5m^4 + 20m^3 + 60m^2 + 120m + 120)$
6	$\frac{e^{-m}}{m^7}(m^6 + 6m^5 + 30m^4 + 120m^3 + 360m^2 + 720m + 720)$
7	$\frac{e^{-m}}{m^8}(m^7 + 7m^6 + 42m^5 + 210m^4 + 840m^3 + 2520m^2 + 5040m + 5040)$
8	$\frac{e^{-m}}{m^9}(m^8 + 8m^7 + 56m^6 + 336m^5 + 1680m^4 + 6720m^3 + 2016m^2 + 4320(m+1))$
9	$\frac{e^{-m}}{m^{10}}(m^9 + 9m^8 + 72m^7 + 504m^6 + 3024m^5 + 15120m^4 + 60480m^3$ $+ 181440m^3 + 36288m + 36288)$

n	$\int_{\lambda}^{\infty} z^n\, e^{-mz/2}\ell n(\frac{z + 1}{z - 1})\, dz$
0	$\frac{2}{m}\left[e^{-m\lambda/2}\ell n(\frac{z+1}{z-1}) - e^{m/2}Ei(-\frac{m}{2}(\lambda+1) + e^{-m/2}Ei(-\frac{m}{2}(\lambda-1))\right]$
1	$\frac{4}{m^2}\left[(1+\frac{m}{2})e^{-m\lambda/2}\ell n(\frac{\lambda+1}{\lambda-1}) - (1-\frac{m}{2})e^{m/2}Ei(-\frac{m}{2}(\lambda+1)) + (1+\frac{m}{2})\right.$ $\left.e^{-m/2}Ei(-\frac{m}{2}(\lambda-1))\right]$

2

$$\frac{16}{m^3}\left[\left(1+\frac{m\lambda}{2}+\frac{m^2\lambda^2}{8}\right)e^{-m\lambda/2}\ln\left(\frac{\lambda+1}{\lambda-1}\right) - \left(1-\frac{m}{2}+\frac{m^2}{8}\right) e^{m/2} Ei\right.$$

$$\left.\left(-\frac{m}{2}(\lambda+1)\right) + \left(1+\frac{m}{2}+\frac{m^2}{3}\right) e^{-m/2} Ei\left(-\frac{m}{2}(\lambda-1)\right)\right]$$

3

$$\frac{96}{m^4}\left[\left(1+\frac{m\lambda}{2}+\frac{m^2\lambda^2}{8}+\frac{m^3\lambda^3}{48}\right) e^{-m\lambda/2}\ln\left(\frac{\lambda+1}{\lambda-1}\right) - \left(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}\right)\right.$$

$$\left. e^{m/2} Ei\left(-\frac{m(\lambda+1)}{2}\right) + \left(1+\frac{m}{2}+\frac{m^2}{8}+\frac{m^3}{48}\right) e^{-m/2} Ei\left(-\frac{m}{2}(\lambda-1)\right)\right]$$

4

$$\frac{24(32)}{m^5}\left[\left(1+\frac{m\lambda}{2}+\frac{m^2\lambda^2}{8}+\frac{m^3\lambda^3}{48}+\frac{m^4\lambda^4}{384}\right) e^{-m\lambda/2}\ln\left(\frac{\lambda+1}{\lambda-1}\right)\right.$$

$$- \left(1-\frac{m}{2}+\frac{m^2}{8}+\frac{m^3}{48}+\frac{m^4}{384}\right) e^{m/2} Ei\left(-\frac{m}{2}(\lambda+1)\right)$$

$$\left.+ \left(1+\frac{m}{2}+\frac{m^2}{8}+\frac{m^3}{48}+\frac{m^4}{384}\right) e^{-m/2} Ei\left(-\frac{m}{2}(\lambda-1)\right)\right]$$

Of the integrals in Eq. (30), the first two are given in Table B-1, and the third in Table 4. Then the integral of Eq. (30) becomes

$$(30.1)\qquad I_{30} = P_1(\mu_2)\ \{Q_1(\lambda_2)\left[\left[\frac{e^{-m\lambda_2/2}(1+\frac{m\lambda_2}{2}) - e^{-m/2}(1+\frac{m}{2})}{3(\frac{m}{2})^2}\right]\right.$$

$$\left.+\frac{6}{(\frac{m}{2})^4}\left[e^{-m/2}(1+\frac{m}{2}+\frac{m^2}{8}+\frac{m^3}{48}) - e^{-m\lambda_2/2}(1+\frac{m\lambda_2}{2}+\frac{m^2\lambda_2^2}{8}+\frac{m^3\lambda_2^3}{48})\right]\right]$$

$$-\frac{2\lambda_2 e^{-m\lambda_2/2}}{(\frac{m}{2})^3}\ (1+\frac{m\lambda_2}{2}+\frac{m^2}{8}(\lambda_2^2-\frac{1}{3})) + \frac{\lambda_2}{2}\left[\frac{96}{m^4}\left[(1+\frac{m\lambda_2}{2}+\frac{m^2\lambda_2^2}{8}+\frac{m^3\lambda_2^3}{48})\right.\right.$$

$$e^{-m\lambda_2/2}\ell n(\frac{\lambda_2+1}{\lambda_2-1})$$

$$-(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48})e^{m/2}Ei(-\frac{m}{2}(\lambda+1)) + (1+\frac{m}{2}+\frac{m^2}{8}+\frac{m^3}{48})e^{-m/2}Ei(-\frac{m}{2}(\lambda-1))$$

$$\left.\left.-\left[(\frac{m^2}{2})\lambda_2+4m\right]\ e^{-m\lambda_2/2}\right]\right] + \frac{\lambda_2}{2}\left[\frac{4}{m^2}\left[(1+\frac{m\lambda_2}{2})e^{-m\lambda_2/2}\ \ell n(\frac{\lambda_2+1}{\lambda_2-1})\right.\right.$$

$$\left.\left.-(1-\frac{m}{2})e^{m/2}Ei(-\frac{m}{2}(\lambda+1)) + (1+\frac{m}{2})e^{-m/2}Ei(-\frac{m}{2}(\lambda-1))\right]\right]\}$$

Since

$$Q_1(\lambda_2) = \frac{\lambda_2}{2}\ \ell n(\frac{\lambda_2+1}{\lambda_2-1}) - 1,$$

expression (30.1) may be evaluated as

$$(30.2)\qquad P_1(\mu)\ \{\frac{\lambda}{2}\left[\ell n\,(\frac{\lambda+1}{\lambda-1}) + Ei\,(-\frac{m}{2}(\lambda-1))\right]\ \left[(D3) - \frac{1}{3}\ (D1)\right] - \left[(D3)\right.$$

$$\left.-\ (D3\lambda) - \frac{1}{3}\ (D1) + (D_{\perp}\lambda)\right]\ + \frac{\lambda}{2}\left[\frac{96}{m^4}\ (1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}) - \frac{4}{3m^2}(1-\frac{m}{2})\right]e^{m/2}$$

$$Ei(-\frac{m}{2}(\lambda+1)) - \frac{8}{m^4}(\frac{m^2\lambda^2}{2} + 4m\lambda)e^{-m\lambda/2} - \lambda\Big[(D2\lambda) - \frac{e^{-m\lambda/2}}{3(\frac{m}{2})}\Big]\}$$

where the notation of Table 4 has been used.

The corresponding B term for k = 1 in Eq. (22) is

$$(31) \qquad I_{31} = P_1(\mu)\int_1^\infty P_1[\lambda(a)]Q_1[\lambda(b)]e^{-m\lambda_1/2}\,d\lambda_1$$

$$(31.1) \qquad I_{31} = P_1(\mu)\ \{(D1)\Big[\ln(\frac{\lambda+1}{\lambda-1}) + Ei(-\frac{m}{2}(\lambda-1)) - \frac{\lambda}{2}\Big[\frac{4}{m^2}(1-\frac{m}{2})$$

$$e^{m/2}\,Ei(-\frac{m}{2}(\lambda+1)) + \frac{e^{-m\lambda/2}}{(\frac{m}{2})}\Big]\}$$

The next term in Eq. (22.5) is

$$(32) \qquad I_{32} = \int_1^\infty P_2[\lambda(a)]Q_2[\lambda(b)]P_2(\mu_2)e^{-m\lambda_1/2}\,(\lambda_1^2 - \frac{1}{3})\,d\lambda_1$$

In the notation of Table 4,

$$(32.1) \qquad I_{32} = P_2(\mu_2)\ \{\frac{Q_2(\lambda_2)}{2}\Big[3[(D4)-(D4\lambda)] - 2[(D2)-(D2\lambda)] + \frac{2}{3m}$$

$$\Big[e^{-m/2} - e^{-m\lambda/2}\Big]\Big]$$

$$+ P_2(\lambda_2)\ \Big[(-\frac{3}{2})\ \Big[\frac{6e^{-m\lambda/2}}{(\frac{m}{2})^4}\ (1+\frac{m\lambda}{2}+\frac{m^2\lambda^2}{8}+\frac{m^3\lambda^3}{48})\Big] + \frac{3}{4}\ \{(D4\lambda)\ \ln(\frac{\lambda+1}{\lambda-1})$$

$$- 24(\frac{32}{m^5})(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}+\frac{m^4}{384})e^{m/2}\ Ei(-\frac{m}{2}(\lambda+1)) + (D4)\ Ei(-\frac{m}{2}(\lambda-1))$$

$$- 24(\frac{32}{m^5})(\frac{m^3}{96}\lambda^2+\frac{m^2\lambda}{8}+\frac{3m}{4})e^{-m\lambda/2}\} - \frac{1}{2}\ \{(D2\lambda)\ \ln(\frac{\lambda+1}{\lambda-1})$$

$$- \frac{16}{m^3}\left(1-\frac{m}{2}+\frac{m^2}{8}\right) e^{m/2}\, Ei\left(-\frac{m}{2}(\lambda+1)\right) + (D2)\, Ei\left(-\frac{m}{2}(\lambda-1)\right) - \frac{8}{m^2}\, e^{-m\lambda/2}\}$$

$$+ \frac{1}{6m}\left\{e^{-m\lambda/2}\, \ell n\left(\frac{\lambda+1}{\lambda-1}\right) - e^{+m/2}\, Ei\left(-\frac{m}{2}(\lambda+1)\right) + e^{-m/2}\, Ei\left(-\frac{m}{2}(\lambda-1)\right)\right\}\Big]\}$$

Now

$$Q_2(\lambda) = \left(\frac{3\lambda^2-1}{4}\right) \ell n\left(\frac{\lambda+1}{\lambda-1}\right) - \frac{3\lambda}{2}\cdot$$

so terms can be combined in the above expression to obtain a simpler form for the integral.

$$(32.2) \qquad P_2(\mu_2)\ \{\left(\frac{3\lambda^2-1}{8}\right) \ell n\left(\frac{\lambda+1}{\lambda-1}\right) \Big[3[(D4)-(D4\lambda)] - 2[(D2)-(D2\lambda)]$$

$$+ \frac{2}{3m}\left[e^{-m/2}-e^{-m\lambda/2}\right] + \frac{3\lambda^2-1}{2}\ \{\left(1+\frac{m\lambda}{2}\right)\frac{e^{-m\lambda/2}}{\left(\frac{m}{2}\right)^2} - \frac{9e^{-m\lambda/2}}{\left(\frac{m}{2}\right)^4}\left(1+\frac{m^2}{2}+\frac{m^2\lambda^2}{8}+\frac{m^3\lambda^3}{48}\right)$$

$$+ \frac{3}{4}(D4\lambda)\ Ei\left(\frac{\lambda+1}{\lambda-1}\right) - 18\left(\frac{32}{m^5}\right)\left(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}+\frac{m^4}{384}\right)e^{m/2}\ Ei\left(-\frac{m}{2}(\lambda+1)\right)$$

$$+ \frac{3}{4}(D4)\ Ei\left(-\frac{m}{2}(\lambda-1)\right) - 18\left(\frac{32}{m^5}\right)\left(\frac{m^3\lambda^2}{96} + \frac{m^2\lambda}{8} + \frac{3m}{4}\right)e^{-m\lambda/2}$$

$$- \frac{1}{2}(D2\lambda)\ \ell n\left(\frac{\lambda+1}{\lambda-1}\right) + \frac{8}{m^3}\left(1-\frac{m}{2}+\frac{m^2}{8}\right)e^{m/2}\ Ei\left(-\frac{m}{2}(\lambda+1)\right)$$

$$- \frac{1}{2}(D2)\ Ei\left(-\frac{m}{2}(\lambda-1)\right) + \frac{8}{m^3}\left(\frac{m}{2}\right)e^{-m\lambda/2} + \frac{e^{-m\lambda/2}}{6m}\ \ell n\left(\frac{\lambda+1}{\lambda-1}\right)$$

$$- \frac{e^{m/2}}{6m}\ Ei\left(-\frac{m}{2}(\lambda+1)\right) + \frac{e^{-m/2}}{6m}\ Ei\left(-\frac{m}{2}(\lambda-1)\right)\}\}$$

Equation (32.2) may be simplified as

$$(32.2) \qquad P_2(\mu)\left[\frac{3\lambda^2-1}{2}\right]\{\left[\frac{3}{4}(D4) - \frac{1}{2}(D2) + \frac{e^{-m/2}}{6m}\right]\left[\ell n\left(\frac{\lambda+1}{\lambda-1}\right) + Ei\left(-\frac{m}{2}(\lambda-1)\right)\right]$$

$$- \left[(18)\left(\frac{32}{m^5}\right)\left(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}+\frac{m^4}{384}\right) - \frac{8}{m^3}\left(1-\frac{m}{2}+\frac{m^2}{8}\right)+\frac{1}{6m}\right] e^{m/2}\, \mathit{Ei}\left(-\frac{m}{2}(\lambda+1)\right)$$

$$+ \frac{e^{-m\lambda/2}}{\left(\frac{m}{2}\right)^2} \left[\frac{(1+m\lambda/2)}{2} - \frac{9(1+m\lambda/2+m^2\lambda^2/8+m^3\lambda^3/48)}{\left(\frac{m}{2}\right)^2} - \frac{144}{m^3}\left(\frac{m^3\lambda^2}{96}+\frac{m^2\lambda}{8}+\frac{3m}{4}\right)+1\right]\}$$

The B_k term for k = 2 is

$$(33) \qquad I_{33} = P_2(\mu_2)\int_1^\infty P_2[\lambda(a)]Q_2[\lambda(b)]e^{-m\lambda_1/2}\, d\lambda_1$$

$$(33.1) \qquad = P_2(\mu_2)\int_1^{\lambda_2} Q_2(\lambda_2)\left(\frac{3\lambda_1^2-1}{2}\right)e^{-m\lambda_1/2}\, d\lambda_1 + P_2(\lambda_2)\int_{\lambda_2}^\infty \left(-\frac{3\lambda_1}{2}\right)e^{-m\lambda_1/2}\, d\lambda_1$$

$$+ P_2(\mu_2)\int_{\lambda_2}^\infty \left[\frac{3\lambda_1^2-1}{4}\right] \ell n\left(\frac{\lambda+1}{\lambda-1}\right) e^{-m\lambda_1/2}\, d\lambda_1\}$$

$$(33.2) \qquad I_{33} = P_2(\mu)\{\ \ell n\left(\frac{\lambda+1}{\lambda-1}\right)\left(\frac{3\lambda^2-1}{8}\right) \left[3(D2)-3(D2\lambda)-(D0)+(D0\lambda)+3(D2\lambda)-(D0\lambda)\right]$$

$$+ \left(\frac{3\lambda^2-1}{8}\right) \left[3(D2)-(D0)\right]\ \mathit{Ei}\left(-\frac{m}{2}(\lambda-1)\right) + \left(\frac{3\lambda^2-1}{8}\right) \left[\frac{48}{m^3}\left(1-\frac{m}{2}+\frac{m^2}{8}\right) - \frac{2}{m}\right]$$

$$e^{m/2}\, \mathit{Ei}\left(-\frac{m}{2}(\lambda+1)\right) - \left(\frac{3\lambda^2-1}{8}\right) \left[\frac{48}{m^3}\left(\frac{m}{2}\right) + 6\left(\frac{4}{m^2}\right)\left(1+\frac{m\lambda}{2}\right)\right] e^{-m\lambda/2}\}$$

If one regroups and cancels terms, Eq. (33.2) becomes

$$(33.3) \qquad I_{33} = P_2(\mu) \left(\frac{3\lambda^2-1}{8}\right)\{\ \{3(D2)-(D0)\}\{\ \ell n\left(\frac{\lambda+1}{\lambda-1}\right) + \mathit{Ei}\left(-\frac{m}{2}(\lambda-1)\right)\}$$

$$- \frac{48}{m^3}\left(1\frac{m}{2}+\frac{m^2}{8}-\frac{m^2}{24}\right) \mathit{Ei}\left(-\frac{m}{2}(\lambda+1)\right) - \frac{24}{m^2}\left(2+\frac{m\lambda}{2}\right)e^{-m\lambda/2}\}$$

Proceeding to the next level of integrals in Eq. (22.5), k = 3, the A term is

$$(34) \qquad I_{34} = \int_1^{\infty} P_3(\mu_2)P_3[\lambda(a)]Q_3[\lambda(b)](\lambda_1^2 - \tfrac{1}{3})e^{-m\lambda_1/2}\, d\lambda_1$$

$$(34.1) \qquad I_{34} = P_3(\mu_2)\ \{\frac{Q_3(\mu_2)}{2}\int_1^{\lambda_2} \left[5\lambda_1^5 - \frac{14}{3}\lambda_1^3 + \lambda_1\right] e^{-m\lambda_1/2}\, d\lambda_1$$

$$+ P_3(\mu_2)\left[\int_{\lambda}^{\infty}\left[\frac{5\lambda_1^5}{4} - \frac{7\lambda_1^3}{6} + \frac{\lambda_1}{4}\right] \ell n(\frac{\lambda+1}{\lambda-1})\ e^{-m\lambda_1/2}\, d\lambda_1\right.$$

$$\left. - \int_{\lambda_2}^{\infty}\left[\frac{5\lambda_1^4}{2} - \frac{3\lambda_1^2}{2} + \frac{2}{9}\right] e^{-m\lambda_1/2}\, d\lambda_1\right]\ \}$$

Again, Tables 4 and B-1 are used to evaluate the integrals of Eq. (34.1). There are at this point nine separate and distinct terms in tthe evaluation of the integral of Eq. (22.5). These are collected in Eq. (22.7) and are further simplified in Eq. (22.8).

$$(22.7) \qquad I_{K1} = P_3(\mu_2)\ \{\frac{Q_3(\lambda_2)}{2}\left[5(D5)-5(D5\lambda)-\frac{14}{3}(D3)+\frac{14}{3}(D3\lambda)+(D1)-(D1\lambda)\right]$$

$$+ \frac{P_3(\lambda_2)}{4}\left[5(D5\lambda)\ \ell n(\frac{\lambda+1}{\lambda-1}) + 5(D5)\ Ei(-\frac{m}{2}(\lambda_2-1))\right.$$

$$- 5(120)(\frac{64}{m^6})(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}+\frac{m^4}{384}-\frac{m^5}{3840})e^{m/2}\ Ei(-\frac{m}{2}(\lambda_2+1))$$

$$\left. - 5(120)(\frac{64}{m^6})(2(\frac{m}{2})^4\lambda^3 + 16(\frac{m}{2})^3\lambda^2 + (\frac{m^2}{2}+72)(\frac{m}{2})^2\lambda + (3m^2+72)(\frac{m}{2}))e^{-m\lambda_2/2}\right]$$

$$- P_3(\lambda_2)\left[\frac{5}{2}(D4\lambda) - \frac{3}{2}(D2\lambda) + \frac{2}{9}(\frac{2}{m})e^{-m\lambda_2/2}\right]$$

$$- \frac{P_3(\lambda_2)}{4}\left[\frac{14}{3}(D3\lambda)\ \ell n(\frac{\lambda_2+1}{\lambda_2-1}) + \frac{14}{3}(D3)\ Ei(-\frac{m}{2}(\lambda_2-1)) - \frac{14}{3}(\frac{96}{m^4})(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48})\right.$$

$$\left. e^{m/2}\ Ei(-\frac{m}{2}(\lambda_2+1)) - \frac{14}{3}(\frac{96}{m^4})(\frac{m^2\lambda_2}{2} + 4m)e^{-m\lambda_2/2}\right]$$

$$+ \frac{P_3(\lambda_2)}{4}\Big[(D1\lambda)\,\ell n\Big(\frac{\lambda_2+1}{\lambda_2-1}\Big) + (D1)\,Ei\Big(-\frac{m}{2}(\lambda_2-1)\Big) - \frac{4}{m^2}\Big(1-\frac{m}{2}\Big)e^{m/2}$$

$$Ei\Big(-\frac{m}{2}(\lambda_2+1)\Big)\Big]\}$$

$$(22.8) \qquad I_{K1} = P_3(\mu_2)\{\frac{P_3(\lambda)}{4}\Big[\{5(D5) - \frac{14}{3}(D3) + (D1)\}\{\ell n\Big(\frac{\lambda+1}{\lambda-1}\Big)$$

$$+ Ei\Big(-\frac{m}{2}(\lambda-1)\Big)\}$$

$$- \{\frac{4}{m^2}\Big(1-\frac{m}{2}\Big) - \frac{14}{3}\Big(\frac{96}{m^4}\Big)\Big(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}\Big) + 700\Big(\frac{64}{m^6}\Big)\Big(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}+\frac{m^4}{384}-\frac{m^5}{3840}\}$$

$$e^{m/2}\,Ei\Big(-\frac{m}{2}(\lambda+1)\Big) - \{700\Big(\frac{64}{m^6}\Big)\Big(\frac{m^4\lambda^3}{8} + 2m^3\lambda^2 + \Big(\frac{m^2}{2}+72\Big)\frac{m^2\lambda}{4}$$

$$+ (3m^2 + 72)\Big(\frac{m}{2}\Big)\Big) - \frac{14}{3}\Big(\frac{96}{m^4}\Big)\Big(\frac{m^2\lambda}{2} + 4m\Big) + \frac{1}{9m}\}\, e^{-m\lambda/2}$$

$$- \{240\Big(\frac{32}{m^5}\Big)\Big(1+\frac{m\lambda}{2}+\frac{m^2\lambda^2}{8}+\frac{m^3\lambda^3}{48}+\frac{m^4\lambda^4}{384}\Big) - \frac{96}{m^3}\Big(1+\frac{m\lambda}{2}+\frac{m^2\lambda^2}{8}\Big)\}\, e^{-m\lambda/2}\Big]$$

$$- \Big(\frac{5\lambda^2}{2} - \frac{2}{3}\Big)\Big[5(D5) - \frac{14}{3}(D3)+(D1)-5(D5\lambda) + \frac{14}{3}(D3\lambda)-(D1\lambda)\Big]\}$$

The B term for k = 3 in Eq. (22.5) becomes

$$(35) \qquad I_{35} = \int_1^\infty P_3(\mu_2)P_3[\lambda(a)]Q_3[\lambda(b)]e^{-m\lambda_1/2}\,d\lambda_1$$

$$(35.1) \qquad I_{35} = P_3(\mu_2)\ \{Q_3(\lambda_2)\int_1^{\lambda_2} P_3(\lambda_1)e^{-m\lambda_1/2}\,d\lambda_1 + P_3(\lambda_2)\int_{\lambda_2}^\infty Q_3(\lambda_1)$$

$$e^{-m\lambda_1/2}\,d\lambda_1\}$$

$$(35.2) \qquad I_{35} = P_3(\mu_2) \left\{ \frac{P_3(\lambda_2)}{4} \left[\{5(D3)-3(D1)\}\{\ell n\left(\frac{\lambda 2+1}{\lambda_2 -1}\right) + \mathcal{E}i\left(-\frac{m}{2}(\lambda_2 -1)\right)\} \right.\right.$$

$$- \left\{\frac{480}{m^4}\left(1-\frac{m}{2}+\frac{m^2}{8}-\frac{m^3}{48}\right) - \frac{12}{m^2}\left(1-\frac{m}{2}\right)\right\} e^{m/2}\, \mathcal{E}i\left(-\frac{m}{2}(\lambda_2+1)\right)$$

$$\left. - \frac{480}{m^4}\left(\frac{m^2\lambda^2}{2} + 4m\right)e^{-m\lambda_2/2} - 10(D2\lambda) - \frac{16}{3m}\, e^{-m\lambda_2/2}\right]$$

$$\left. - \left(\frac{5\lambda_2^2}{2} - \frac{2}{3}\right)\left[5(D3)-5(D3\lambda)-3(D1)+3(D1\lambda)\right]\right\}$$

At this point, the desired level of approximation for the K_{gu5} integral has been reached. It is now necessary to take the terms developed in Eq. (22)—(35) and include these, with the proper coefficients, in Eq. (22.6), for I_{K1} and carry out the integration over the second set of coordinates. Thus

$$(17.5.5.1) \qquad K_{gu5} = \int I_{K1}(\chi_a(2)\chi_b'(2) - \chi_a'(2)\chi_b(2))\, dV_2$$

is the integral that must be solved.

At the present level of approximation, the μ coordinate appears in the factor I_{K1} only through $P_i(\mu)$, the i^{th} Legendre polynomial. One property of these Legendre polynomials is that each contains only even or odd powers of the argument, as i is even or odd. This property allows some simplifications for the K_{gu5} integral.

Note that

$$(36) \qquad \chi_a(2)\chi_b'(2) - \chi_a'(2)\chi_b(2) = \frac{\sqrt{\alpha^3\gamma^3}}{\pi}\left[e^{-\alpha r_a}e^{-\gamma r_b} - e^{-\gamma r_a}e^{-\alpha r_b}\right]$$

$$(36.1) \qquad = \frac{\sqrt{\alpha^3\gamma^3}}{\pi}\left[e^{-(\alpha+\gamma)R\lambda/2}\right]\left[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right]$$

The second wavefunction is an odd function. Since the integral over μ is carried out between symmetric limits,

$$(37) \qquad \int_{-1}^{1} \left[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right] P_i(\mu)d\mu = 0$$

and

$$(38) \qquad \int_{-1}^{1} \left[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right] P_i(\mu)\mu^2 d\mu = 0$$

for even values of i. Thus the even terms in the expansion for I_{K1} contribute nothing to the final integral.

The lowest term remaining which contributes to the K_{gu5} integral, after combining terms (see Eqs. (30.2) and (31.1) for individual term values) is

$$(39) \qquad I_{39} = 2\sqrt{\alpha^3\gamma^3}\, R^2 P_1(\mu)\Big\{\left[\frac{48A_1}{m^4}\left(1-\frac{m^2}{72}+\left(1-\frac{m^2}{72}\right)\left(\frac{m}{2}\right)+\frac{m^2}{8}+\frac{m^3}{48}\right)-\frac{2B_1}{m^2}\left(1+\frac{m}{2}\right)\right]$$

$$\lambda e^{-m/2}\left[\ln\left(\frac{\lambda+1}{\lambda-1}\right) + Ei\left(-\frac{m}{2}(\lambda-1)\right)\right] - \left[\frac{48A_1}{m^4}\left(1-\frac{m^2}{72}-\left(1-\frac{m^2}{72}\right)\left(\frac{m}{2}\right)+\frac{m^2}{8}-\frac{m^3}{48}\right)\right.$$

$$\left.-\frac{2B_1}{m^2}\left(1-\frac{m}{2}\right)\right]\lambda e^{m/2}\, Ei\left(-\frac{m}{2}(\lambda+1)\right) + \frac{48}{m^4}\left[A_1\left(4-\frac{m^2}{6}\right) - B_1\left(\frac{m^2}{6}\right)\right] e^{-m\lambda/2}$$

$$- \left[\frac{96A_1}{m^4}\left(1-\frac{m^2}{72}+\left(1-\frac{m^2}{72}\right)\left(\frac{m}{2}\right)+\frac{m^2}{8}+\frac{m^3}{48}\right) - \frac{4B_1}{m^2}\left(1+\frac{m}{2}\right)\right] e^{-m/2}\Big\}$$

Equation (39) may be simplified by letting

$$(40) \qquad T_{11} = \left[\frac{48A_1}{m^4}\left(1-\frac{m^2}{72}+\left(1-\frac{m^2}{72}\right)\left(\frac{m}{2}\right)+\frac{m^2}{8}+\frac{m^3}{48}\right) - \frac{2B_1}{m^2}\left(1+\frac{m}{2}\right)\right]$$

$$(41) \quad T_{12} = \left[\frac{48A_1}{m^4}\left(1-\frac{m^2}{72}-\left(1-\frac{m^2}{72}\right)\left(\frac{m}{2}\right)+\frac{m^2}{8}-\frac{m^3}{48}\right) - \frac{2B_1}{m^2}\left(1-\frac{m}{2}\right)\right]$$

Equation (39) then becomes

$$(39.1) \quad I_{39} = 2\sqrt{\alpha^3\gamma^3}\; R^2 P_1(\mu)\; \{T_{11} e^{-m/2}\lambda\left[\ell n\left(\frac{\lambda+1}{\lambda-1}\right) + Ei\left(-\frac{m}{2}(\lambda-1)\right)\right]$$

$$- T_{12}\lambda e^{m/2}\; Ei\left(-\frac{m}{2}(\lambda+1)\right) + \frac{48}{m^4}\left[A_1\left(4-\frac{m^2}{6}\right) - B_1\left(\frac{m^2}{6}\right)\right] e^{-m\lambda/2}$$

$$- 2T_{11} e^{-m/2}\}$$

To complete the calculation of the first term in K_{gu5}, integration must be performed over the remaining electron coordinates:

$$(42) \quad \frac{\sqrt{\alpha^3\gamma^3}\; R^3}{4} \int_{-1}^{1}\int_{1}^{\infty} (\lambda - \mu)\left[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right] e^{-(\alpha+\gamma)R\lambda/2} I_{K1}\, d\lambda\, d\mu$$

Consider the μ integral first. $P_1(\mu) = \mu$, so

$$(43) \quad \int_{-1}^{1} (\lambda^2-\mu^2)\left[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right] \mu\, d\mu = 2(\lambda^2 B_{gu} - C_{gu})$$

where

$$(44) \quad B_{gu} = \left(\frac{1}{2}\right)\int_{-1}^{1} \mu\left[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right] d\mu$$

$$(44.1) \quad B_{gu} = -\frac{e^{-(\alpha-\gamma)R/2}(1+(\alpha-\gamma)R/2) + e^{(\alpha-\gamma)R/2}((\alpha-\gamma)R/2-1)}{(\alpha-\gamma)^2R^2/4}$$

and

$$(45) \qquad C_{gu} = (\tfrac{1}{2}) \int_{-1}^{1} \mu^3 \left[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right] d\mu$$

$$(45.1) \qquad C_{gu} = + \frac{e^{(\alpha-\gamma)R/2}}{(\alpha-\gamma)^4R^4/16} \left[6 - 3(\alpha-\gamma)R + \frac{3}{4}(\alpha-\gamma)^2R^2 - \frac{(\alpha-\gamma)^3R^3}{8}\right]$$

$$- \frac{e^{-(\alpha-\gamma)R/2}}{(\alpha-\gamma)^4R^4/16} \left[6 + 3(\alpha-\gamma)R + \frac{3}{4}(\alpha-\gamma)^2R^2 + \frac{(\alpha-\gamma)^3R^3}{8}\right]$$

With these definitions, the integral over λ can be obtained:

$$(43.1) \qquad \alpha^3\gamma^3R^5\int_1^{\infty} \left[\lambda^2B_{gu}-C_{gu}\right] e^{-m\lambda/2} \{T_{11}e^{-m/2}\lambda \left[\ell n(\frac{\lambda+1}{\lambda-1}) + Ei\ (-\frac{m}{2}(\lambda-1))\right]$$

$$- T_{12}\ e^{m/2}\ Ei(-\frac{m}{2}(\lambda+1)) + \frac{48}{m^4}\left[A_1(4-\frac{m^2}{6}) - B_1(\frac{m^2}{6})\right] e^{-m\lambda/2}$$

$$- 2T_{11}e^{-m/2}\}\ d\lambda$$

$$(43.2) \qquad \alpha^3\gamma^3R^5\ \{B_{gu}\int_1^{\infty}T_{11}e^{-m/2}\lambda^3 \left[\ell n(\frac{\lambda+1}{\lambda-1}) + Ei(-\frac{m}{2}(\lambda-1))\right] e^{-m\lambda/2}d\lambda$$

$$- B_{gu}\int_1^{\infty}T_{12}e^{m/2}\lambda^3\ Ei(-\frac{m}{2}(\lambda+1))e^{-m\lambda/2}d\lambda - 2B_{gu}\int_1^{\infty}T_{11}e^{-m/2}e^{-m\lambda/2}\lambda^2d\lambda$$

$$+ B_{gu}\int_1^{\infty}(\frac{48}{m^4})e^{-m\lambda/2}\left[A_1(4-\frac{m^2}{6}) - B_1(\frac{m^2}{6})\right] \lambda^2e^{-m\lambda/2}d\lambda$$

$$- C_{gu}\int_1^{\infty}T_{11}e^{-m/2}\lambda \left[\ell n(\frac{\lambda+1}{\lambda-1}) + Ei(-\frac{m}{2}(\lambda-1))\right] e^{-m\lambda/2}d\lambda$$

$$+ C_{gu}\int_1^{\infty} T_{11}e^{m/2}\lambda e^{-m\lambda/2}\ Ei(-\frac{m}{2}(\lambda+1))d\lambda \quad +2C_{gu}\int_1^{\infty} T_{11}e^{-m/2}\ e^{-m\lambda/2}\ d\lambda$$

$$- \quad C_{gu}\int_1^{\infty}(\frac{48}{m^4})\ \{A_1(4-\frac{m^2}{6}) - B_1(\frac{m^2}{6})\}\ e^{-m\lambda}\ d\lambda \quad \}$$

The majority of the integrals of Eq. (43.4) appear in Tables B-1 and 4. The remaining integrals will now be evaluated in steps (44)—(52).

$$(44) \qquad I_E = \int_1^\infty \lambda^3 e^{-m\lambda/2}\, \mathcal{E}i(-\tfrac{m}{2}(\lambda-1))\,d\lambda$$

To integrate by parts, let

$$dv = \lambda^3 e^{-m\lambda/2} d\lambda$$

$$v = -\frac{96}{m^4}\, e^{-m\lambda/2} \left[(\tfrac{m}{2})^3 \frac{\lambda^3}{6} + (\tfrac{m}{2})^2 \frac{\lambda^2}{2} + \frac{m\lambda}{2} + 1\right]$$

$$u = \mathcal{E}i(-\tfrac{m}{2}(\lambda-1))$$

$$du = \frac{e^{-m/2\,(\lambda-1)}}{(\lambda-1)}$$

Integral I_E may then be replaced by

$$(44.1) \qquad I_E = [uv]_1^\infty - \int_1^\infty vdu$$

Noting that $\mathcal{E}i(-\frac{m}{2}(\lambda-1))$ cannot be evaluated at the lower limit and replacing this by $\lim\limits_{\delta\to 1} \mathcal{E}i(-\frac{m}{2}(\beta-1))$, Eq. (44.1) becomes

$$(44.2) \qquad I_E = \lim_{\delta\to 1} \{\frac{96}{m^4}\, e^{-m/2}\, (\frac{m^3}{48} + \frac{m^2}{8} + \frac{m}{2} + 1)\, \mathcal{E}i(-\tfrac{m}{2}(\delta-1))$$

$$+ \frac{96}{m^4} \int_\delta^\infty e^{-m\lambda/2} \left[\frac{m^3\lambda^3}{48} + \frac{m^2\lambda^2}{8} + \frac{m\lambda}{2} + 1\right] \frac{e^{-m/2\,(\lambda-1)}}{(\lambda-1)}\, d\lambda\}$$

Consider now the remaining integral of Eq. (44.2). This integral can be evaluated by making a change of variables, $\lambda - 1 = z$.

$$(45) \quad I_{45} = \frac{96}{m^4} e^{-m/2} \int_{\delta-1}^{\infty} \frac{e^{-mz}}{z} \left[\frac{m^3}{48} (z^3-3z^2+3z-1) + \frac{m^2}{8} (z^2-2z+1) + \frac{m}{2} (z-1) + 1\right] dz$$

$$(45.1) \quad I_{45} = \frac{96}{m^4} e^{-m/2} \left[(\frac{m^2}{16} + \frac{5m}{16} + \frac{2}{3}) - (1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}) \; Ei(-m(\delta-1))\right]$$

The insertion of the result of Eq. (45.1) into Eq. (44.2) yields

$$(44.3) \quad \frac{96}{m^4} e^{-m/2} (\frac{m^2}{16} + \frac{5m}{16} + \frac{2}{3}) + \lim_{\delta\to1} (\frac{96}{m^4} e^{-m/2})(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}) \left[Ei(-\frac{m}{2}(\delta-1)) - Ei(-m(\delta-1))\right]$$

Step (44.3) has to be substituted back into Eq. (43.2). In Eq. (43.2) the integral over $\ln (\frac{\lambda+1}{\lambda-1})$ must be evaluated before proceeding to the limit. The value for the $\ln (\frac{\lambda+1}{\lambda-1})$ integral is

$$(46) \quad \frac{96}{m^4} \{e^{-m/2}(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}) \lim_{\delta\to1} \left[\ln(2) - \ln(\delta-1) + Ei(-\frac{m}{2}(\delta-1))\right] - (1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}) e^{-m/2} Ei(-m) - \frac{1}{3}\left[\frac{m^2}{4} + (\frac{3m}{2} + 1)(\frac{m}{2})\right] e^{-m/2}$$

Thus the first term in the K_{gu5} integral (Eq. (17.3.5.1), including coefficients, is

$$(47) \quad B_{gu} T_{11} \left(\frac{96}{m^4}\right) e^{-m} \left\{\frac{m^2}{16} + \frac{5m}{16} + \frac{2}{3} - e^{-m} \left(1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}\right) Ei(-m)\right.$$

$$+ e^{-m}\left(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}\right) \lim_{\delta\to1} \left[\ln(2) - \ln(\delta-1) + 2\, Ei\left(- \frac{m}{2}(\delta-1)\right)\right.$$

$$\left.\left. - Ei(-m(\delta-1))\right]\right\}$$

The last term in Eq. (47) has already been evaluated in Appendix B, and has the limiting value

$$C + \ln\left(\frac{m}{2}\right) - \ln(2) + \ln(2)$$

giving a final value for Eq. (47) of

$$(47.1) \quad B_{gu} T_{11} \left(\frac{96}{m^4}\right)\left[e^{-m}\left(\frac{m^2}{16} + \frac{5m}{16} + \frac{2}{3}\right) - \left(1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}\right) Ei(-m)\right.$$

$$\left.+ e^{-m}\left(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}\right)\left(C + \ln\left(\frac{m}{2}\right)\right)\right]$$

The corresponding term in Eq. (43) with coefficient C_{gu} may be solved in an identical manner, with a final result of

$$(48) \quad C_{gu} T_{11} \left(\frac{4}{m^2}\right)\left[\frac{e^{-m}}{2} - \left(1 - \frac{m}{2}\right) Ei(-m) + e^{-m}\left(1 + \frac{m}{2}\right)\left(C + \ln\left(\frac{m}{2}\right)\right)\right]$$

The integrals of the $Ei(- \frac{m}{2}(\lambda+1))$ terms of Eq. (43.2) will be considered next. The approach, as above, is by an integration by parts:

$$(49) \quad I_{E1} = \int_1^\infty \lambda^3 e^{-m\lambda/2}\, Ei\left(- \frac{m}{2}(\lambda+1)\right)d\lambda$$

Let

$$dv = \lambda^3 e^{-m\lambda/2} d$$

$$v = \left(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8} + \frac{m^3\lambda^3}{48}\right)\left(\frac{96}{m^4}\right) e^{-m\lambda/2}$$

$$u = Ei\left(- \frac{m}{2}(\lambda+1)\right)$$

$$du = \frac{e^{-m/2(\lambda+1)}}{(\lambda+1)} d\lambda$$

This gives

$$(49.1) \qquad I_{E1} = \left(\frac{96}{m^4}\right) e^{-m/2} \left(\frac{m^3}{48} + \frac{m^2}{8} + \frac{m}{2} + 1\right) Ei(-m)$$

$$+ \int_1^\infty \left(\frac{96}{m^4}\right) e^{-m\lambda/2} \left(\frac{m^3\lambda^3}{48} + \frac{m^2\lambda^2}{8} + \frac{m\lambda}{2} + 1\right) \frac{e^{-m/2(\lambda+1)}}{(\lambda-1)} \; d\lambda$$

The remaining term in Eq. (49.1) is integrated by making the substitution λ + 1 = z.

$$(50) \qquad \frac{96}{m^4} e^{+m/2} \int_2^\infty \frac{e^{-mz}}{z} \left[\frac{m^3}{48} (z^3 - 3z^2 + 3z - 1) + \frac{m^2}{8} (z^2 - 2z + 1)\right.$$

$$\left. + \frac{m}{2} (z - 1) + 1\right] dz$$

$$= \frac{96}{m^4} e^{+m/2} \int_2^\infty e^{-mz} \left[z^2\left(\frac{m^3}{48}\right) + z\left(\frac{m^2}{8}\right)\left(1 - \frac{m}{2}\right) + \frac{m}{2}\left(1 - \frac{m}{2} + \frac{m^2}{8}\right)\right.$$

$$\left. + \left(1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}\right)\left(\frac{1}{z}\right)\right] dz$$

$$= \frac{96}{m^4} e^{m/2} \left[(\frac{m^3}{48}) \frac{2e^{-2m}}{m^3} (1+2m+2m^2) + (\frac{m^2}{8})(1 - \frac{m}{2}) \frac{e^{-2m}}{m^2}(1 + 2m) \right.$$

$$\left. (\frac{m}{2})(1 - \frac{m}{2} + \frac{m^2}{8}) \frac{e^{-2m}}{m} \right] - \frac{96e^{m/2}}{m^4} (1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}) \mathit{Ei}(-2m)$$

Combination of like terms and multiplication of this integral by its coefficient in the K_{gu5} term yields the final result

$$(51) \qquad T_{12}B_{gu} e^{+m/2} \{\frac{96}{m^4} \left[e^{-m/2} (1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}) \mathit{Ei}(-m) \right.$$

$$\left. - (1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}) e^{+m/2} \mathit{Ei}(-2m) \right] + \frac{16}{m^4} (\frac{m^2}{8} + \frac{m}{8} + 4) e^{-3m/2}\}$$

Identical techniques give the solution of the equivalent C_{gu} integral of Eq. (43.4)

$$(52) \qquad T_{12}C_{gu} \int_1^{\infty} e^{m/2} \lambda e^{-m\lambda/2} \mathit{Ei}(- \frac{m}{2}(\lambda+1)) d\lambda$$

$$(52.1) \qquad = T_{12}C_{gu} \{\frac{4}{m^2} (1 + \frac{m}{2}) \mathit{Ei}(-m) + \frac{2e^{-m}}{m^2} - \frac{4e^{m}}{m^2} (1 - \frac{m}{2}) \mathit{Ei}(-2m)\}$$

The remaining integrals of Eq. (43.2) are tabulated in Tables B-1 and 4.

Substitution of these terms into Eq. (43.2) gives the first non-zero contribution to the K_{gu5} integral. As the integrals were to be used in a computer program for finding the numerical value of the energy as a function of internuclear separation, no additional simplification was attempted with this integral.

The next term which yields a non-zero contribution is the k = 3 term in I_{K1} of Eq. (17.3.5.1). The integral multiplying the coefficient B_3 in Eq. (22.6) is

$$(53) \qquad I_{53} = \sqrt{\alpha^3\gamma^3}\, R^2 P_3(\mu) \{ \frac{P_3(\lambda)}{4} \Big[\{5(D3) - 3(D1)\} \{\ln(\frac{\lambda+1}{\lambda-1}) + Ei(-\frac{m}{2}(\lambda-1))\}$$

$$- \{\frac{30(16)}{m^4} (1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}) - \frac{12}{m^2} (1 - \frac{m}{2})\} e^{m/2}\, Ei(-\frac{m}{2}(\lambda+1))$$

$$- \{\frac{30(16)}{m^4} (\frac{m^2\lambda}{2} + 4m)\} e^{-m\lambda/2} - 10(D2\lambda) - \frac{16}{3m} e^{-m\lambda/2} \Big] - \Big[\frac{5\lambda^2}{2} - \frac{2}{3}\Big]$$

$$\Big[5(D3) - 3(D1) - \frac{30(16)}{m^4} \{(1 - \frac{m^2}{120}) + (1 - \frac{m^2}{120})(\frac{m}{2}) + \frac{m^2\lambda^2}{8} + \frac{m^3\lambda^3}{48}\}$$

$$e^{-m\lambda/2}\Big]\}$$

Proceed by again considering the μ integral in Eq. (17.5.5.1) ueing Eq. (53) and (32.6). Now

$$(54) \qquad \int_{-1}^{1} (\lambda^2 - \mu^2) P_3(\mu) \Big[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\Big]\, d\lambda = \lambda^2 B_{gu3} + C_{gu3}$$

where B_{gu3} and C_{gu3} are determined in Eqs. (55) and (56), respectively.

$$(55) \qquad B_{gu3} = (\frac{1}{2}) \int_{-1}^{1} (5\mu^3 - 3\mu) \Big[e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\Big]\, d\mu$$

$$(55.1) \qquad B_{gu3} = 5 \Big[\frac{(\alpha-\gamma)^3R^3}{8} - \frac{3(\alpha-\gamma)^2R^2}{4} + 3(\alpha-\gamma)R + 6\Big] \frac{e^{(\alpha-\gamma)R/2}}{(\alpha-\gamma)^4R^4/16}$$

$$- 5 \Big[\frac{(\alpha-\gamma)^3R^3}{8} + \frac{3(\alpha-\gamma)^2R^2}{4} + 3(\alpha-\gamma)R + 6\Big] \frac{e^{-(\alpha-\gamma)R/2}}{(\alpha-\gamma)^4R^4/16}$$

$$- 3 \left[\frac{(\alpha-\gamma)R}{2} - 1\right] \frac{e^{(\alpha-\gamma)R/2}}{(\alpha-\gamma)^2R^2/4} + 3 \left[\frac{(\alpha-\gamma)R}{2} + 1\right] \left(\frac{1}{(\alpha-\gamma)^2R^2/4}\right) e^{-(\alpha-\gamma)R/2}$$

The integrals required for evaluating B_{gu3} are listed in Table B-1. Similarly, C_{gu3} is

$$\text{(56)} \quad C_{gu3} = \frac{1}{2}\int_{-1}^{1} \left[3\mu^3 - 5\mu^5\right] \left(e^{-(\alpha-\gamma)R\mu/2} - e^{(\alpha-\gamma)R\mu/2}\right) d\lambda$$

$$\text{(56.1)} \quad C_{gu3} = \frac{48}{(\alpha-\gamma)^4R^4}\{\left[\frac{(\alpha-\gamma)^3R^3}{8} - \frac{3(\alpha-\gamma)^2R^2}{4} + 3(\alpha-\gamma)R - 6\right] e^{(\alpha-\gamma)R/2}$$

$$- \left[\frac{(\alpha-\gamma)^3R^3}{8} + \frac{3(\alpha-\gamma)^2R^2}{4} + 3(\alpha-\gamma)R + 6\right] e^{-(\alpha-\gamma)R/2}\}$$

$$- \frac{320}{(\alpha-\gamma)^6R^6} \{\Bigg[\frac{(\alpha-\gamma)^5R^5}{32} - \frac{5(\alpha-\gamma)^4R^4}{16} + \frac{5(\alpha-\gamma)^3R^3}{2} - 15(\alpha-\gamma)^2R^2$$

$$+ 60(\alpha-\gamma)R - 120\Bigg] e^{(\alpha-\gamma)R/2} + \Bigg[\frac{(\alpha-\gamma)^5R^5}{32} + \frac{5(\alpha-\gamma)^4R^4}{16} + \frac{5(\alpha-\gamma)^3R^3}{2}$$

$$+ 15(\alpha-\gamma)^2R^2 + 60(\alpha-\gamma)R - 120\Bigg] e^{-(\alpha-\gamma)R/2}\}$$

With these definitions, the integral of Eq. (54) can now be evaluated by integrating over the final coordinate. The integral of Eq. (54) is

$$\text{(54.1)} \quad \frac{\alpha^3\gamma^3R^5}{2} \int_1^\infty \left[\lambda^2 B_{gu} + C_{gu3}\right] e^{-m\lambda/2}\{\frac{P_3(\lambda)}{4} \Bigg[\{5(D3) - 3(D1)\}$$

$$\{ \ln\left(\frac{\lambda+1}{\lambda-1}\right) + Ei\left(- \frac{m}{2}(\lambda - 1)\right)\} - \{\frac{30(16)}{m^4}\left(1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}\right) - \frac{12}{m^2}\left(1 - \frac{m}{2}\right)\}$$

$$\times \quad e^{m/2}\ Ei\left(- \frac{m}{2}(\lambda+1)\right) - \{\frac{30(16)}{m^4} \left(\frac{m^2\lambda}{2} + 4m\right)\} e^{-m\mu/2} - 10(D2\lambda) - \frac{16}{3m} e^{-m\mu/2}\Bigg]$$

$$- (\frac{5\lambda^2}{2} - \frac{2}{3}) \left[5(D3) - 3(D1) - \frac{480}{m^4} \quad \{(1 - \frac{m^2}{120}) + (1 - \frac{m^2}{120})(\frac{m\lambda}{2}) \right.$$

$$\left. + \frac{m^2\lambda^2}{8} + \frac{m^3\lambda^3}{48} \} \quad e^{-m\lambda/2} \right] \} \, d\lambda$$

For convenience, let

(57) $$T_{13} = 5(D3) - 3(D1)$$

(58) $$T_{14} = \left[\frac{480}{m^4} (1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}) - \frac{12}{m^2} (1 - \frac{m}{2}) \right] e^{m/2}$$

The integral of Eq. (54.1), on substituting for $P_3(\lambda)$, becomes

(54.2) $$\frac{\alpha^3\gamma^3R^5}{2} \int_1^\infty (\lambda^2 B_{gu3} + C_{gu3}) \{(\frac{5\lambda^3-3}{8})T_{13} \left[\ell n(\frac{\lambda+1}{\lambda-1}) + Ei(- \frac{m}{2}(\lambda-1)) \right]$$

$$- (\frac{5\lambda^3-3\lambda}{8})T_{14} \; Ei(- \frac{m}{2}(\lambda+1)) + (\frac{5\lambda^2}{2} - \frac{2}{3})\{ \left[5(D3\lambda)-3(D1\lambda) \right]$$

$$- \left[\frac{5}{2}(D2\lambda) - \frac{4e^{-m\lambda/2}}{3m} \right] \} - (\frac{5\lambda^2}{2} - \frac{2}{3})T_{13} - (\frac{5\lambda^3-3\lambda}{2}) \; \frac{20}{m^4}(\frac{m^2\lambda}{2} + 4m)e^{-m\lambda/2} \}$$

$$e^{-m\lambda/2} d\lambda$$

Each term in the integral of Eq. (54.2) will be evaluated separately. Taking these in order,

(59) $$I_{59} = T_{13}\int_1^\infty (\frac{5\lambda^3-3\lambda}{8}) \left[\ell n (\frac{\lambda+1}{\lambda-1}) + Ei (- \frac{m}{2}(\lambda-1)) \right] e^{-m\lambda/2} d\lambda$$

(59.1) $$I_{59} = \lim_{\delta \to 1} \frac{5T_{13}}{8} \{ (D3) [\ell n (2) - \ell n (\delta-1)] - \frac{96}{m^4}(1- \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}) \, e^{m/2} \, Ei(-m)$$

$$+ (D3) \, Ei (- \frac{m}{2}(\delta-1)) - \frac{96}{m^4} (\frac{m^2}{2} + 4m)e^{-m/2} \}$$

$$+ \frac{5T_{13}}{8} \int_{1}^{\infty} \lambda^{3}\, Ei(- \frac{m}{2}(\lambda-1))d\lambda - \lim_{\delta\to 1} \frac{3T_{13}}{8} \{(D1)[\ln(2) - \ln(\delta-1)]$$

$$- \frac{4}{m^{2}} (1-\frac{m}{2})\, e^{m/2}\, Ei(-m) + (D1)\, Ei(- \frac{m}{2}(\delta-1))$$

$$- \frac{3T_{13}}{8} \int_{1}^{\infty} \lambda\, Ei(- \frac{m}{2}(\lambda-1))d\lambda\}$$

The Ei integrals of Eq. (59.1) can be integrated by parts. In the first integral, let

$$dv = \lambda^{3} e^{-m\lambda/2} d\lambda$$

$$v = - \frac{96}{m^{4}}\, e^{-m\lambda/2}(1 + \frac{m\lambda}{2} + \frac{m^{2}\lambda^{2}}{8} + \frac{m^{3}\lambda^{3}}{48})$$

$$u = Ei(- \frac{m}{2}(\lambda-1))$$

$$du = \frac{e^{-m/2(\lambda-1)}}{(\lambda-1)}$$

With this, the $Ei(- \frac{m}{2}(\lambda-1))\lambda^{3}$ integral in Eq. (59.1) becomes

(60) $$I_{59} = \lim_{\delta\to 1} \{\frac{96}{m^{4}}\, e^{-m/2}(1+\frac{m}{2}+\frac{m^{2}}{8}+\frac{m^{3}}{48}) Ei(- \frac{m}{2}(\delta-1))$$

$$+ \frac{96}{m^{4}} \int_{1}^{\infty} (\frac{m^{3}\lambda^{3}}{48} + \frac{m^{2}\lambda^{2}}{8} + \frac{m\lambda}{2} + 1)\, e^{-m\lambda/2}\, \frac{e^{-m/2(\lambda-1)}}{(\lambda-1)}\, d\lambda \quad \}$$

In the last integral, let $z = \lambda - 1$.

$$(61)\quad \frac{96}{m^4}\, e^{-m/2} \int_1^\infty \left[\frac{m^3}{48}\, z^2 + \frac{m^2}{8}(1+\frac{m}{2})\, z + \frac{m}{2}(1+\frac{m}{2}+\frac{m^2}{8})\right] e^{-mz}dz$$

$$+ \frac{96}{m^4}\, e^{-m/2} \int_1^\infty \left[1+\frac{m}{2}+\frac{m^2}{8}+\frac{m^3}{48}\right] (\frac{1}{z})\, e^{-mz}dz$$

The first of these integrals in Eq. (61) is equal to

$$(62)\quad \frac{96}{m^4}\, e^{-m/2} \left[\frac{1}{12} + \frac{1}{8}\,(1+\frac{m}{2}) + \frac{1}{2}(1 + \frac{m}{2} + \frac{m^2}{8})\right]$$

and the second is equal to

$$(63)\quad -\frac{96}{m^4}\, e^{-m/2}\, (1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48})\; Ei(-m(\delta-1))$$

By similar methods, the other integral over $Ei(-\frac{m}{2}(\lambda-1)$ in Eq. (59.1) is evaluated.

$$(64)\quad \lim_{\delta\to 1} \left[\frac{4}{m^2}\, e^{-m/2}\, (1+\frac{m}{2})\, Ei(-\frac{m}{2}(\delta-1)) + \frac{2e^{-m/2}}{m^2}\right.$$

$$\left. - \frac{4e^{-m/2}}{m^2}\, (1+\frac{m}{2})\, Ei(-\, m\, (\delta-1))\right]$$

Noting that the coefficient of those terms which are ill-behaved at the lower limit in Eqs. (59.1), (63) and (64) is the same for each pair of integrals, the discontinuity can be reduced to evaluating

$$(65)\quad \lim_{\delta\to 1} \left[-\ln(\delta-1) + 2\ln(-\frac{m}{2}(\delta-1)) - \ln(-m(\delta-1))\right]$$

This is the same term which is evaluated in Appendix B; its value is

$$(65.1) \qquad -\ell n(2) + \ell n(\tfrac{m}{2}) + C$$

Using this result in each of the two pair of ill-behaved terms of Eqs. (60), (63), and (64),

$$(60.1) \qquad I_{59} = \frac{5}{8} C_{gu3} T_{13} \{ (D3) [\ell n(\tfrac{m}{2}) + C] - \frac{16}{m^4} e^{m/2} (1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}) Ei(-m)$$

$$+ \frac{16 e^{-m/2}}{m^4} \left[\frac{3m^2}{8} + \frac{15m}{8} + 4 - 4m - \frac{m^2}{2} \right] \} - \frac{3}{8} C_{gu3} T_{13} \{ (D1) [Ei(\tfrac{m}{2}) + C]$$

$$- \frac{4e^{m/2}}{m} (1 - \frac{m}{2}) Ei\,(-m) + \frac{2e^{-m/2}}{m^2} \}$$

Taking the integral over $\lambda^2 B_{gu3}$ in Eq. (54.2) next, the same sequence of steps is followed.

$$(66) \qquad I_{66} = \int_1^\infty \lambda^5 \left[\ell n(\frac{\lambda+1}{\lambda-1}) + Ei(-\frac{m}{2}(\lambda-1)) \right] e^{-m\lambda/2}\, d\lambda$$

$$(66.1) \qquad I_{66} = \int_1^\infty \lambda^5\ \ell n(\frac{\lambda+1}{\lambda-1})\ e^{-m\lambda/2}\, d\lambda + \int_1^\infty \lambda^5\ Ei(-\frac{m}{2}(\lambda-1))\ e^{-m\lambda/2}\, d\lambda$$

The first integral on the right-hand side of Eq. (66.1) may be evaluated, using Table B-1. It is found to have the value

$$(67) \qquad \lim_{\delta \to 1} \{ (D5) [\ell n(2) - \ell n(\delta-1)] + (D5)\ Ei(-\frac{m}{2}(\delta-1)) - \frac{120(64)}{m^6}$$

$$\Big[(1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48} + \frac{m^4}{384} - \frac{m^5}{3840})\, e^{m/2}\, Ei(-m)$$

$$+ (\frac{m^4}{8} + 2m^3 + (\frac{m^2}{2} + 72)(\frac{m^2}{4}) + (3m^2 + 72)(\frac{m}{2}))\, e^{-m/2} \Big]$$

The other integral in Eq. (66) can then be integrated by parts, with

$$dv = \lambda^5\, e^{-m\lambda/2}\, d\lambda$$

$$v = \frac{-120e^{-m\lambda/2}}{(\frac{m}{2})^6} (1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8} + \frac{m^3\lambda^3}{48} + \frac{m^4\lambda^4}{384} + \frac{m^5\lambda^5}{3840})$$

$$u = Ei(- \frac{m}{2}(\lambda-1))$$

$$du = e^{-m/2(\lambda-1)}\, \frac{d\lambda}{(\lambda-1)}$$

It is found that

$$(68) \qquad I_{68} = \int_1^\infty \lambda^5 e^{-m\lambda/2}\, Ei(- \frac{m}{2}(\lambda-1))\, d\lambda$$

$$= \lim_{\delta\to 1} \{\frac{120(64)e^{-m/2}}{m^6} (1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48} + \frac{m^4}{384} + \frac{m^5}{3840})\, Ei(- \frac{m}{2}(\delta-1))\}$$

$$+ \frac{120(64)}{m^6} \int_1^\infty e^{-m\lambda/2} (1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8} + \frac{m^3\lambda^3}{48} + \frac{m^4\lambda^4}{384} + \frac{m^5\lambda^5}{3840})\, \frac{e^{-m(\lambda-1)/2}}{(\lambda-1)}\, d\lambda$$

The terms in Eq. (68) are then evaluated, yielding

$$(68.1) \qquad I_{68} = \frac{(120)(64)e^{-m/2}}{m^6} \Big[\frac{1}{160} + \frac{1}{64}(1+\frac{m}{2}) + \frac{1}{24}(1+\frac{m}{2}+\frac{m^2}{8})$$

$$+ \frac{1}{8} \left(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48}\right) + \frac{1}{2}\left(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48} + \frac{m^4}{384}\right)\Bigg]$$

$$- \frac{120(64)e^{-m/2}}{m^6} \lim_{\delta\to1}\left(1 + \frac{m}{2} + \frac{m^2}{8} + \frac{m^3}{48} + \frac{m^4}{384} + \frac{m^5}{3840}\right) Ei\left(- \frac{m}{2}(\delta-1)\right)$$

Combination of Eq. (68.2) and Eq. (60.1) gives the value of I_{59} in Eq. (59.1) as

$$\text{(59.2)} \quad B_{gu3}T_{13} \Bigg\{\frac{5}{8} \Bigg[(D5)\left(\ln\left(\frac{m}{2}\right)+C\right) - \frac{120(64)}{m^6} e^{m/2} \left(1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}\right.$$

$$\left. + \frac{m^4}{384} - \frac{m^5}{3840}\right) Ei(-m) + \frac{64e^{-m/2}}{m^6} \left(- \frac{m^4}{4} - \frac{7m^3}{2} - 18m^3 - 36m + \frac{3}{4} + \frac{15}{8}\left(1+\frac{m}{2}\right)\right.$$

$$\left. + \frac{5}{2}\left(2+m+\frac{m^2}{4}\right) + \frac{5}{2}\left(6 + 3m + \frac{3m^2}{4} + \frac{m^3}{8}\right) + \frac{5}{2}\left(24 + 12m + 3m^2 + \frac{m^3}{2} + \frac{m^4}{16}\right)\right)\Bigg]$$

$$- \frac{3}{8} \Bigg[(D3)\left(\ln\left(\frac{m}{2}\right)+C\right) - \frac{96}{m^4} e^{m/2} \left(1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48}\right) Ei(-m)$$

$$+ \frac{16e^{-m/2}}{m^4} \left(4 + \frac{15m}{8} + \frac{3m^2}{8} - \frac{m^2}{2} - 4m\right)\Bigg]\Bigg\}$$

The next of the major terms in Eq. (54.2) are presented in Eqs. (69)—(74.2). This term is

$$\text{(69)} \quad T_{14} \int_1^{\infty}\left(\frac{5\lambda^3-3\lambda}{8}\right)(\lambda^2B_{gu3} + C_{gu3}) e^{-m\lambda/2} Ei\left(- \frac{m}{2}(\lambda+1)\right) d\lambda$$

The method of solution will be similar to that used on the ill-behaved integrals just considered. i.e., expansion by parts followed by a substitution of variables.

$$(69.1) \quad I_{69} = \int_1^\infty (5\lambda^3 - 3\lambda)\, e^{-m\lambda/2}\, Ei(-\tfrac{m}{2}(\lambda+1))\, d\lambda$$

$$= 5 \int_1^\infty \lambda^3\, e^{-m\lambda/2}\, Ei(-\tfrac{m}{2}(\lambda+1))\, d\lambda - 3 \int_1^\infty \lambda\, e^{-m\lambda/2}\, Ei(-\tfrac{m}{2}(\lambda+1))\, d\lambda$$

$$(69.2) \quad I_{69} = 5 \Big[(D3)\, Ei(-m) + \frac{16 e^{-3m/2}}{m^4} \left(\frac{m^2}{8} + \frac{m}{2} + 4\right) - \frac{96\, e^{-m/2}}{m^4} (1 - \frac{m}{2}$$

$$+ \frac{m^2}{8} - \frac{m^3}{48}) Ei(-2m) \Big] - 3 \Big[(D1)\, Ei(-m) + \frac{2e^{-3m/2}}{m^2} - \frac{2e^{m/2}}{m^2} (1 + \tfrac{m}{2})\, Ei(-2m) \Big]$$

Similarly,

$$(70) \quad 5 \int_1^\infty \lambda^5\, e^{-m\lambda/2}\, Ei(-\tfrac{m}{2}(\lambda+1))\, d\lambda - 3 \int_1^\infty \lambda^3\, e^{-m\lambda/2}\, Ei(-\tfrac{m}{2}(\lambda+1))\, d\lambda$$

$$(70.1) \quad = 5 \Big[(D5)\, Ei(-m) + \frac{64 e^{-3m/2}}{m^6} (\frac{m^4}{2} + m^3 + \frac{3m^2}{2} + \frac{3m}{2} + \frac{3}{4}$$

$$+ \tfrac{5}{2}(1 - \tfrac{m}{2}) (m^3 + \frac{3m^2}{2} + \frac{3m}{2} + \frac{3}{4}) + 5(2 - m + \frac{m^2}{4})(m^2 + m + \frac{1}{2})$$

$$+ \tfrac{5}{2}(1+2m)(6 - 3m + \frac{3m^2}{4} - \frac{m^3}{8}) + \tfrac{5}{2}(24 - 12m + 3m^2 - \frac{m^3}{2} + \frac{m^4}{16}))$$

$$- \frac{64(120)}{m^6} (1 - \frac{m}{2} + \frac{m^2}{8} - \frac{m^3}{48} + \frac{m^4}{384} - \frac{m^5}{3840})\, e^{m/2}\, Ei(-2m) \Big]$$

$$- 3 \Big[(D3)\, Ei(-m) + \frac{16 e^{-3m/2}}{m^4} \left(\frac{m^2}{8} + \frac{m}{8} + 4\right) - \frac{96 e^{m/2}}{m^4} (1 - \frac{m}{2} + \frac{m^2}{8}$$

$$- \frac{m^3}{48})\, Ei(-2m) \Big]$$

The next term in Eq. (54.2) is

$$(71) \quad \int_1^\infty (\lambda^2 B_{gu3} + C_{gu3})\left(\frac{5\lambda^2}{2} - \frac{2}{3}\right)\left[5(D3\lambda) - 3(D1\lambda)\right] e^{-m\lambda/2}\, d\lambda$$

$$(71.1) \quad = \frac{5}{2} B_{gu3} \left(\frac{80}{m^4}\right) \int_1^\infty \lambda^4\left(6 + 3m\lambda + \frac{3m^2\lambda^2}{4} + \frac{m^3\lambda^3}{8}\right) e^{-m\lambda}\, d\lambda$$

$$- \frac{5}{2} B_{gu3} \left(\frac{12}{m^2}\right) \int_1^\infty \lambda^4\left(1 + \frac{m\lambda}{2}\right) e^{-m\lambda}\, d\lambda + \left(\frac{5}{2} C_{gu3} - \frac{2}{3} B_{gu3}\right) \int_1^\infty \frac{80}{m^4}\left(6 + 3m\lambda\right.$$

$$\left. + \frac{3m^2\lambda^2}{4} + \frac{m^3\lambda^3}{8}\right) \lambda^2 e^{-m\lambda}\, d\lambda + \left(\frac{5}{2} C_{gu3} - \frac{2}{3} B_{gu3}\right)\left(\frac{12}{m^2}\right) \int_1^\infty e^{-m\lambda}\left(\lambda^2 + \frac{m\lambda^3}{2}\right) d\lambda$$

$$- \frac{2}{3} C_{gu3} \left(\frac{80}{m^4}\right) \int_1^\infty \left(6 + 3m\lambda + \frac{3m^2\lambda^2}{4} + \frac{m^3\lambda^3}{8}\right) e^{-m\lambda}\, d\lambda$$

$$+ \frac{2}{3} C_{gu3} \left(\frac{12}{m^2}\right) \int_1^\infty \left(1 + \frac{m\lambda}{2}\right) e^{-m\lambda}\, d\lambda$$

These integrals are tabulated in Table 4. Using the terms defined there and rearranging the result algebraically yields the form

$$(71.2) \quad \frac{B_{gu3}}{4} \left\{25 \left[\frac{2}{m}(C7) + \frac{12}{m^2}(C6) + \frac{48}{m^3}(C5) + \frac{96}{m^4}(C4)\right]\right.$$

$$- 15 \left[\frac{4}{m^2}(C4) + \frac{2}{m}(C5)\right] - \frac{20}{3} \left[\frac{2}{m}(C5) + \frac{12}{m^2}(C4)\right]$$

$$\left. - \frac{20}{3} \left[\frac{48}{m^3}(C3) + \frac{96}{m^4}(C2)\right] + 4 \left[\frac{4}{m^2}(C2) + \frac{2}{m}(C3)\right]\right\}$$

$$+ \frac{C_{gu3}}{4} \left\{25 \left[\frac{2}{m}(C5) + \frac{12}{m^2}(C4) + \frac{48}{m^3}(C3) + \frac{96}{m^4}(C2)\right]\right.$$

$$- 15 \left[\frac{4}{m^2}(C2) + \frac{2}{m}(C3)\right] - \frac{20}{3} \left[\frac{2}{m}(C3) + \frac{12}{m^2}(C2) + \frac{48}{m^3}(C1) + \frac{96}{m^4}(C0)\right]$$

$$\left. + 4 \left[\frac{4}{m^2}(C0) + \frac{2}{m}(C1)\right]\right\}$$

The next term to be considered in Eq. (54.2) also has its component integrals given in Table 4:

$$(72) \quad \int_1^\infty \frac{5}{2} B_{gu3} \quad \lambda^3 \{ (\frac{40}{m})(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8}) - \frac{4}{3m} \} e^{-m\lambda} \, d\lambda$$

$$+ (\frac{5C_{gu3} - 3B_{gu3}}{2}) \int_1^\infty \lambda^2 \left[(\frac{40}{m^3})(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8}) - \frac{4}{3m} \right] e^{-m\lambda} \, d\lambda$$

$$- \frac{3}{2} C_{gu3} \int_1^\infty \lambda \left[(\frac{40}{m^3})(1 + \frac{m\lambda}{2} + \frac{m^2\lambda^2}{8}) - \frac{4}{3m} \right] e^{-m\lambda} \, d\lambda$$

If Eq. (72) is evaluated by use of the tabulated integrals and combining terms, its value is

$$(72.1) \quad B_{gu3} \left[\frac{25}{2m}(C7) + \frac{50}{m^2}(C6) + (\frac{100}{m^3} - \frac{65}{6m})(C5) - \frac{30}{m^2}(C4) \right.$$

$$\left. - (\frac{60}{m^3} - \frac{2}{m})(C3) \right] + C_{gu3} \left[\frac{25}{2m}(C5) + \frac{50}{m^2}(C4) + (\frac{100}{m^3} - \frac{65}{6m})(C3) \right.$$

$$\left. - \frac{30}{m^2}(C2) - (\frac{60}{m^3} - \frac{2}{m})(C1) \right]$$

The next term from Eq. (54.2) is

$$(73) \quad I_{73} = T_{13} \int_1^\infty (\frac{5\lambda^2}{2} - \frac{2}{3})(\lambda^2 B_{gu3} + C_{gu3}) \, e^{-m\lambda/2} \, d\lambda$$

$$= T_{13} (\frac{5B_{gu3}}{2}) \int_1^\infty \lambda^4 \, e^{-m\lambda/2} \, d\lambda + T_{13} (\frac{5C_{gu3}}{2} - \frac{2B_{gu3}}{3}) \int_1^\infty \lambda^2 \, e^{-m\lambda/2} \, d\lambda$$

$$- \frac{2C_{gu3}}{3} T_{13} \int_1^\infty e^{-m\lambda/2} \, d\lambda$$

Equation (73) is evaluated as

$$(73.1) \qquad I_{73} = \frac{5B_{gu3}}{2} T_{13}(D4) + T_{13} \left(\frac{5C_{gu3}}{2} - \frac{2B_{gu3}}{3}\right)(D2) - \frac{2C_{gu3}}{3} T_{13}(D0)$$

The final term in Eq. (54.2) is

$$(74) \qquad \int_1^\infty \left(\frac{5\lambda^3-3\lambda}{2}\right) \left[\frac{20}{m^4}\left(\frac{m^2\lambda}{2} + 4m\right)\right] (\lambda^2 B_{gu3} + C_{gu3})\, e^{-m\lambda/2}\, d\lambda$$

Referring to Table 4 for the solutions to these integrals, and rearranging, the final result becomes

$$(74.1) \qquad B_{gu3} \left[\frac{25}{m^2}(C6) - \frac{15}{m^2}(C4) + \frac{100}{m^3}(C5) - \frac{120}{m^3}(C3)\right]$$

$$+ C_{gu3} \left[\frac{25}{m^2}(C4) - \frac{15}{m^2}(C2) + \frac{100}{m^3}(C3) - \frac{120}{m^3}(C1)\right]$$

Substitution of Eqs. (59.2), (67), (68.1), (69.3), (70.1), (71.2), (72.1), (73.1), and (74.1) into (54.2) yields the next term in the series for Eq. (17.3.5.1). As the calculation of the energy was to be done numerically on a digital computer, each term was used in the form presented above without explicit back-substitution.

From comparison of the final value of the K_{gu} term with values at T = 1 given by Huzinaga (49), and for large R, it was determined that this was a sufficient number of terms to give an overall accuracy which was adequate for the calculation of the ground state, varying at worst by only about five percent from the best numerical solutions available. The work involved in adding additional terms to improve the accuracy of this integral (the only one where any approximation has been necessary) did not seem commensurate with the improvement in accuracy attainable with the additional terms. For the smallest values of R considered, the total contribution of this term was less than one-tenth of the total energy, dropping to less than five percent in the range of internuclear separations of interest, so the error involved in this truncation was small.

The final determination of the ground state energy curve was accomplished by using a computer program to evaluate the terms given above in Eq. (11) for values of R, the internuclear separation, from 0.2 to 15.0 Bohr. The screening constants α and γ were chosen at each value of R to produce a minimum in the energy curve. The basic scheme used by the program was to first select an R value, and then to compute, term-by-term, the value of the various interactions for values of α ranging from $\sqrt{2}$ to 2, the range appropriate to the screening constant for hydrogen. From a consideration of the physical meaning of the screening constant, it is evident that the values of γ appropriate to the problem are between 0 and $\sqrt{2}$, as the value $\alpha = \gamma = \sqrt{2}$ gives a minimum in the energy curve for large R. This corresponds physically to the equivalence of the two electrons in a hydride ion (H^-). The program then recalculates the energy for another pair of α and γ values, finally storing the energy minimum and the values of α and γ corresponding to this minimum. Since this portion of the calculation was to be achieved by use of the computer, no attempt was made to further combine terms beyond the level presented earlier. In hindsight, it is evident that there would have been some virtue in having combined terms further: for small values of R, round-off errors began to be a considerable factor in the calculations on the computer. This was particularly evident in the evaluation of the $Ei(-x)$ terms, where double precision calculations were necessary, in the evaluation of $\ell n(\frac{m}{2})$ and C, and in the highest of the terms in the K_{gu5} integral, where the problem of round off was never completely eliminated. This problem was an additional inducement to truncate the series at the point chosen, as it was evident that the problem would continue to be a troublesome one for the even more involved higher power terms. Had it been possible, extended precision (21 or more decimals) would have avoided the worst of the problems encountered with round off, but the computing facilities currently available do not support this arithmetic.

One additional word concerning the programs is in order. Some effort was made to reduce the time required per run of the program, which would have taken some two to four hours of computer time for evaluating the ground state energy for R values spaced 0.05 Bohr apart. This was achieved partially by first determining the rough curve shape, and then by selecting R values which were widely spaced in regions where the energy curve was smooth, using closely spaced values only in regions of large curvature. This allowed a great reduction in machine usage, but necessitated a somewhat more involved program for plotting the results.

C. RESULTS OF MOLECULAR ION CALCULATIONS

The ground state energy of the doubly negative hydrogen molecular ion can be calculated using the functions developed in Section IV B. The details of the results are given here. Five cases will be considered separately; these illustrate effectively the results obtained and indicate the levels of accuracy in the calculations. Of these cases, two are chosen primarally to determine the accuracy of the numerical results by comparison with previously known values, and a third is chosen for the insight which it sheds on the results obtained for the doubly negative ion ground state. These will be considered in the following order: neutral hydrogen ground state with fixed and then with variable screening, the doubly negative ion with and without variations in the screening, and then the He_2 ground state, for comparison with the results for the K_{gu} interactions.

Case I. Neutral Hydrogen with Constant Screening

The ground state energy of the neutral hydrogen molecule was determined using the previously developed terms for comparison with known results, to verify the accuracy of these terms. The calculation is derivable from that of the doubly negative ion by the presence of only two electrons in the molecular orbitals. The value obtained for this energy as a function of internuclear separation is given as Fig. 10. Note that the energy approached asymptotically is not the anticipated value of -2 Rydbergs, but is $(-2.0 + \frac{5}{8})$ Rydbergs. To obtain the value of -2 Rydbergs requires that the molecule separate into two neutral atoms. However, in the MO approach, the molecule may also separate into

$H^+ + H^-$. Such a system differs in internal energy from the $H^0 + H^0$ system by the calculated $(\frac{5}{8})$ Rydberg. This point is discussed in Slater(51) in great detail, and the result of the present calculations are in agreement with the values given by Slater for this approach. The screening constant α has the value $\sqrt{2}$.

For finite internuclear separations, the values found by this calculation are close to those obtained by the best available wavefunction choice (52), and for small separation, will be about as good as can be obtained for a simple wavefunction choice, wherein the screening constant is held fixed.

Case II. Neutral Hydrogen with Variable Screening

In order to obtain more accurate energy values, the screening parameter may be varied with separation by choosing values for the parameter to minimize the calculated energy at each separation R. As seen in Fig. 11, the behaviour at infinity is improved, although it still shows the behaviour characteristic of MO calculations. Figure 12 shows the variation of the screening parameter with internuclear separation for the calculations of Fig. 11. This variation of the screening parameter is characteristic of this system (51); as the electron "orbit" will be that predicted by the Bohr model for infinite internuclear separation, and will gradually lessen its distance from the center of the nuclei as the two nuclei approach each other closely. This leads to an increase in the screening parameter with decreasing distance (as the screening parameter is inversely proportional to the separation of the electron from the nucleus). The energy minimum

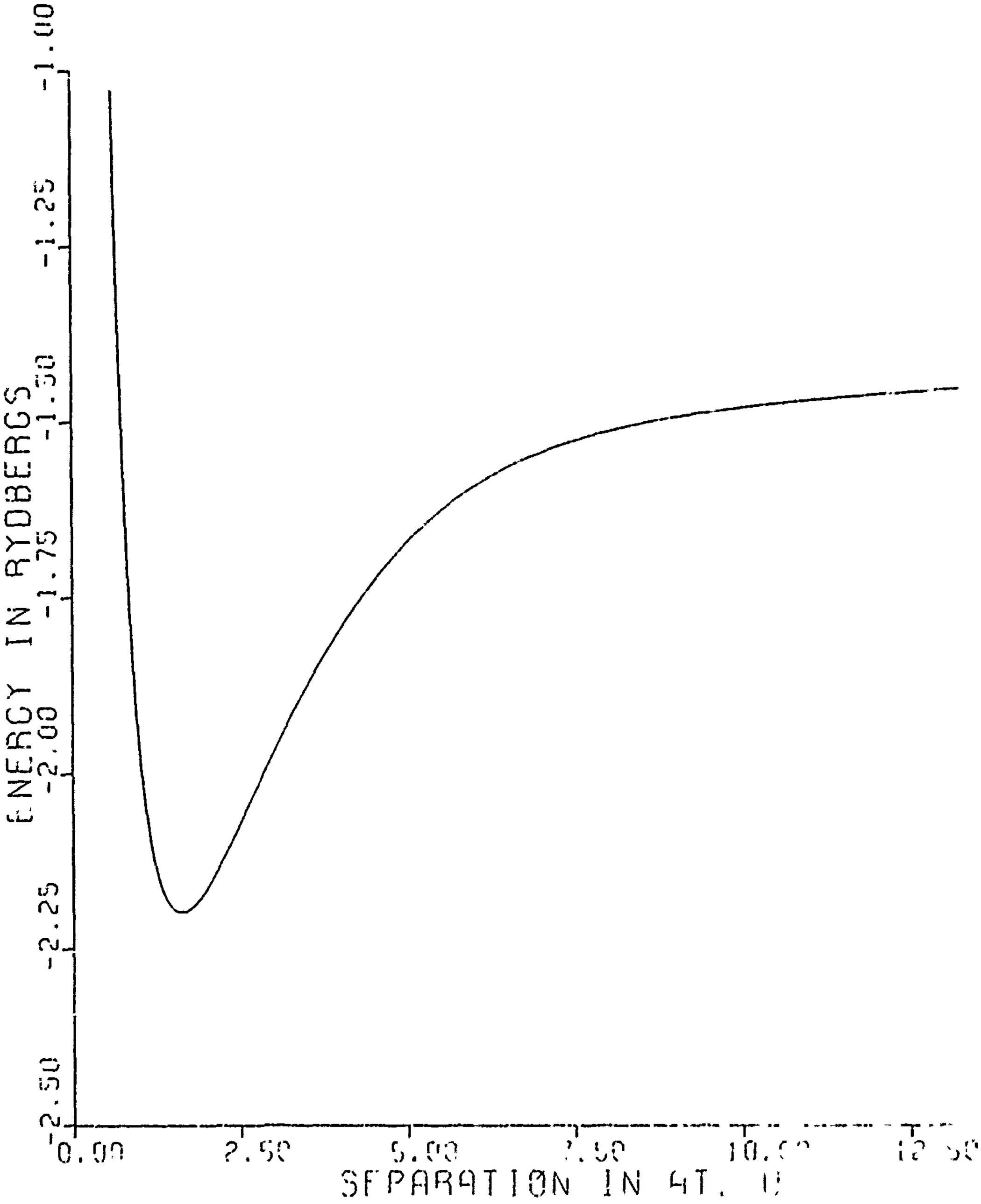


Fig. 10. Neutral Hydrogen with Fixed Screening.

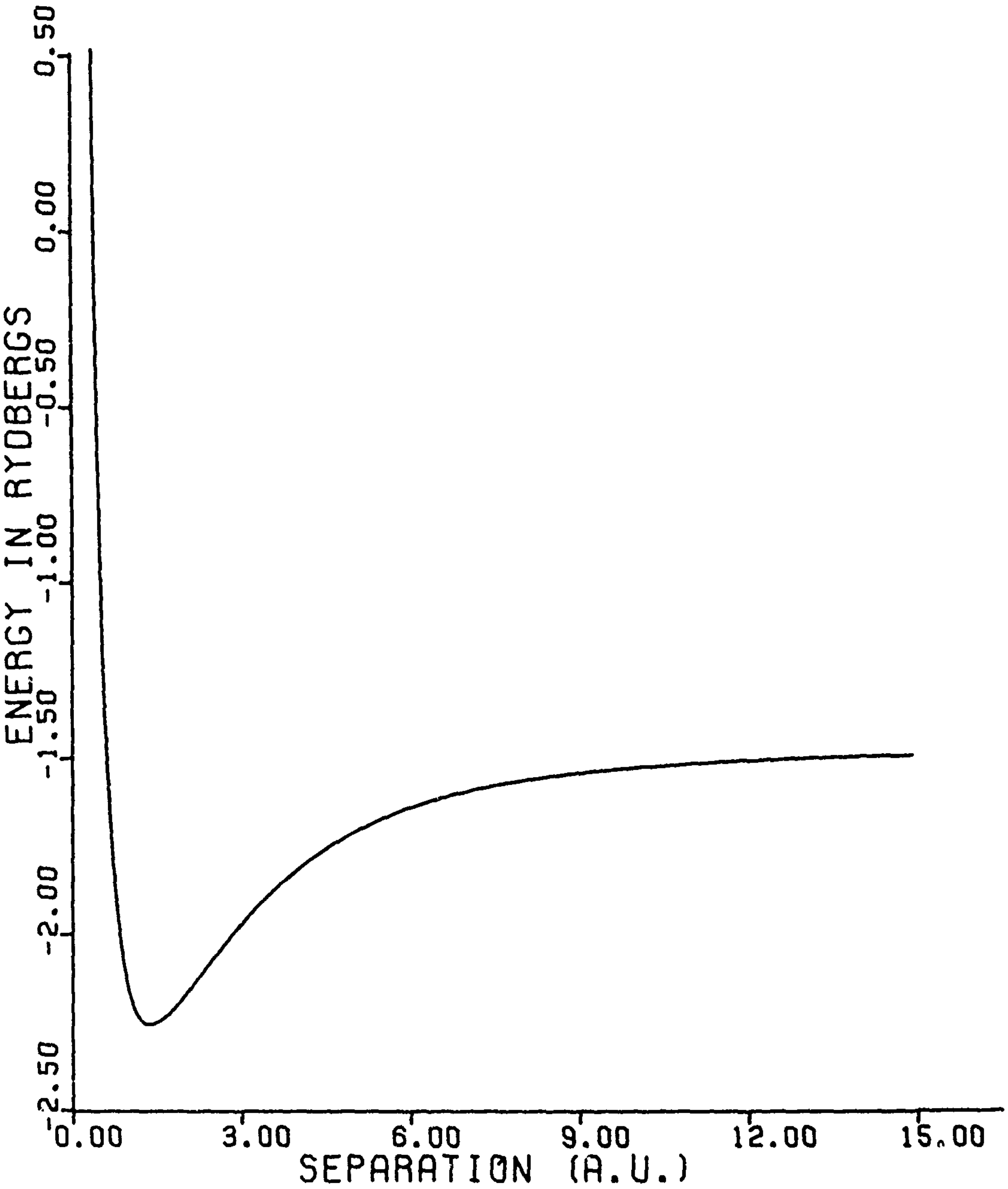


Fig. 11 H_2 neutral ground state energy with variable screening.

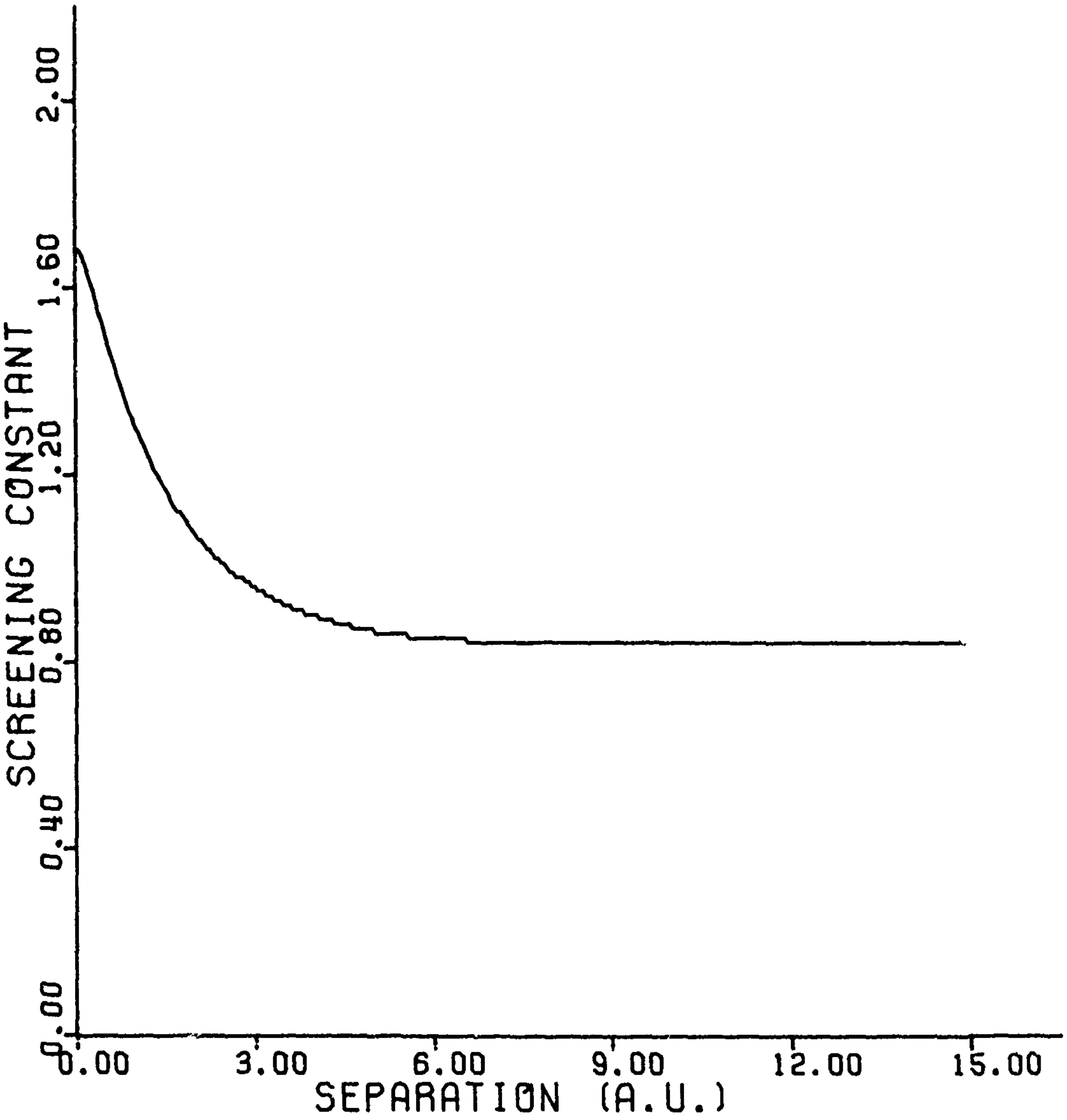


Fig. 12. Screening constant vs. internuclear separation for H_2.

obtained by this approach, -2.27 Rydbergs, is consistent with the better values given by MO calculations cited by Slater (51). Values obtained by Wang (53) by a similar method give an energy minimum of -2.278 Rydbergs. In each case, the position of the energy minimum is at about 1.4 Bohr internuclear separation.

The above comparisons with previous work on the neutral hydrogen molecule were performed to test the validity of the present computation scheme. The transition from the four-electron calculation of the H_2^{-2} molecular ion to the two-electron H_2 molecule involves contraction of the state function, but individual terms remain unaltered.

Case III. H_2^{-2} Ground State Energy with Fixed Screening

If the electrons in the two types of orbitals are equivalent (i.e., have the same screening constant), the curve of the energy as a function of internuclear separation, shown in Fig. 13, does not possess a minimum for finite values of the internuclear separation. The screening constants used for calculating this curve ($\alpha=\gamma=\sqrt{2}$) were chosen to give the lowest energy for infinite separation of the two nuclei. At small separations, the energy is everywhere above that of the neutral hydrogen molecule. Indeed, the energy of the H_2^{-2} is greater than that of the separate H^- ions removed to infinity. Thus the curve of Fig. 13 actually lies in the range of free states of the neutral molecule (see Fig. 11). As the separation tends toward infinity, the energy of the H_2^{-2} drops below that of the neutral molecule; this is in accord with the known stability of the Hydride (H^-) ion. The energy obtained for very large R values agrees acceptably with the known binding energy of the

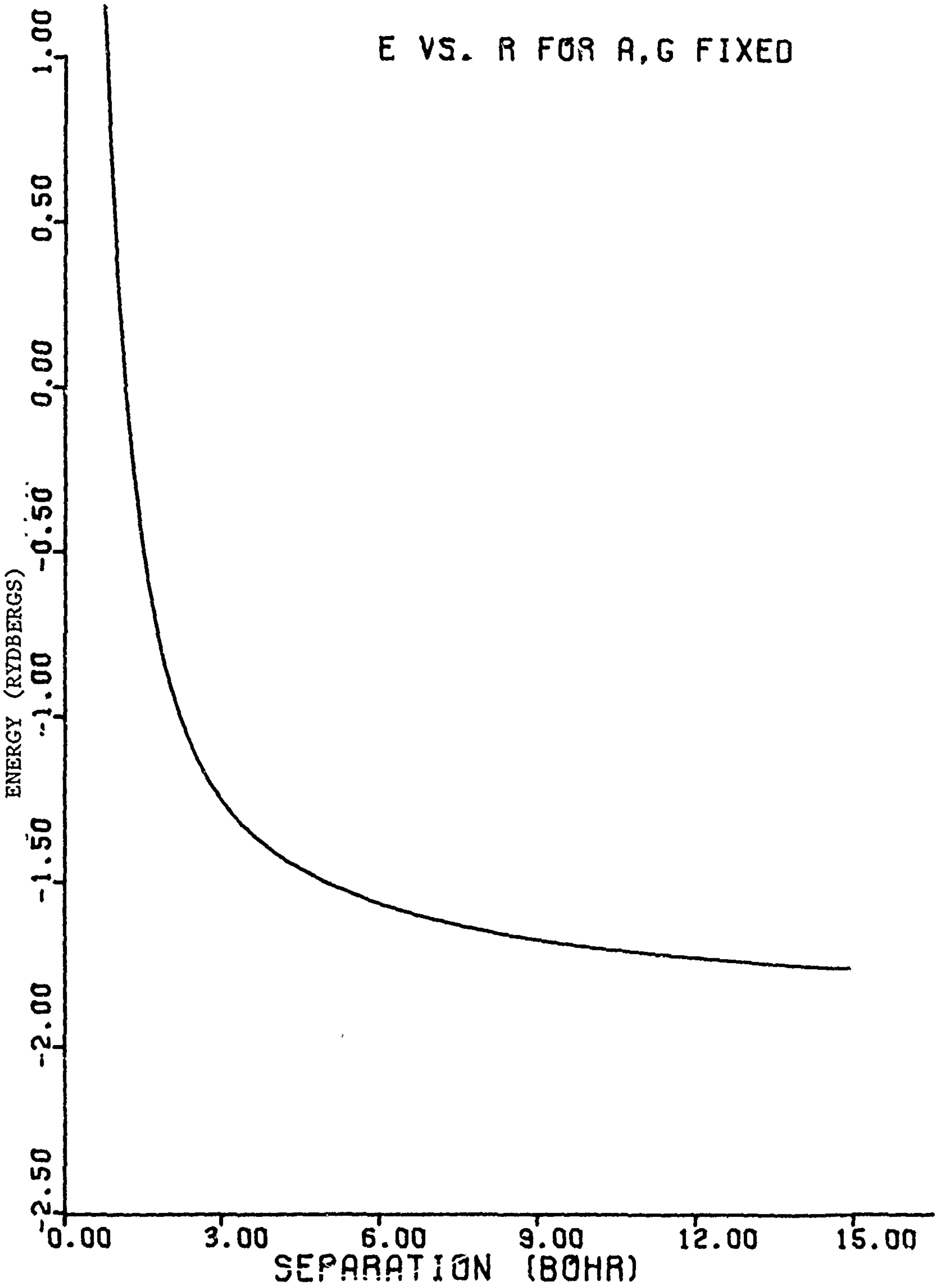


Fig. 13. Ground state energy for the doubly negative hydrogen molecular ion with fixed screening.

excess electron of the Hydride ion. The asymptotic energy of the H_2^{-2} system should, on the basis of the single hydride ion calculation of Chandrasekhar (55), be about 2.05 Rydbergs. The present value of 1.85 Rydbergs is in accord with the asymptotic results using similar techniques and wavefunctions obtained by Fischer-Hjalmars (48) for the H_2^{-1} ground state. The values reported there for the equivalent method (her Method II) give the results of 1.85 Rydbergs for the asymptotic value of the energy.

Case IV. Doubly Negative Hydrogen Molecular IOn with Variable Screening

The next set of curves, Figs. 14, 15, and 16, illustrate the results obtained for the hydrogen molecular ion when the screening parameters are allowed to vary with R. Figure 14 gives the ground state energy for the molecular ion as a function of internuclear separation. Figure 15 gives the screening parameters corresponding to the energy curve of Fig. 14. Of more importance, however, is the behaviour of the curve in the region about 7 Bohr. Figure 16, which is a composite of Figs. 11, 13, and 14, shows that the energy curve of Fig. 16 is actually a composite of the two curves of Figs. 11 and 13, with a transition occurring at the point where the two curves cross.

The behaviour of the screening constants alpha and gamma also gives insight into what is happening. It will be noted that the shape of the variation of alpha with separation in Fig. 15 is much the same as for the parameter if Fig. 12, with alpha increasing smoothly with decreasing separation. In Case III (H_2^{-2}), the two constants were held

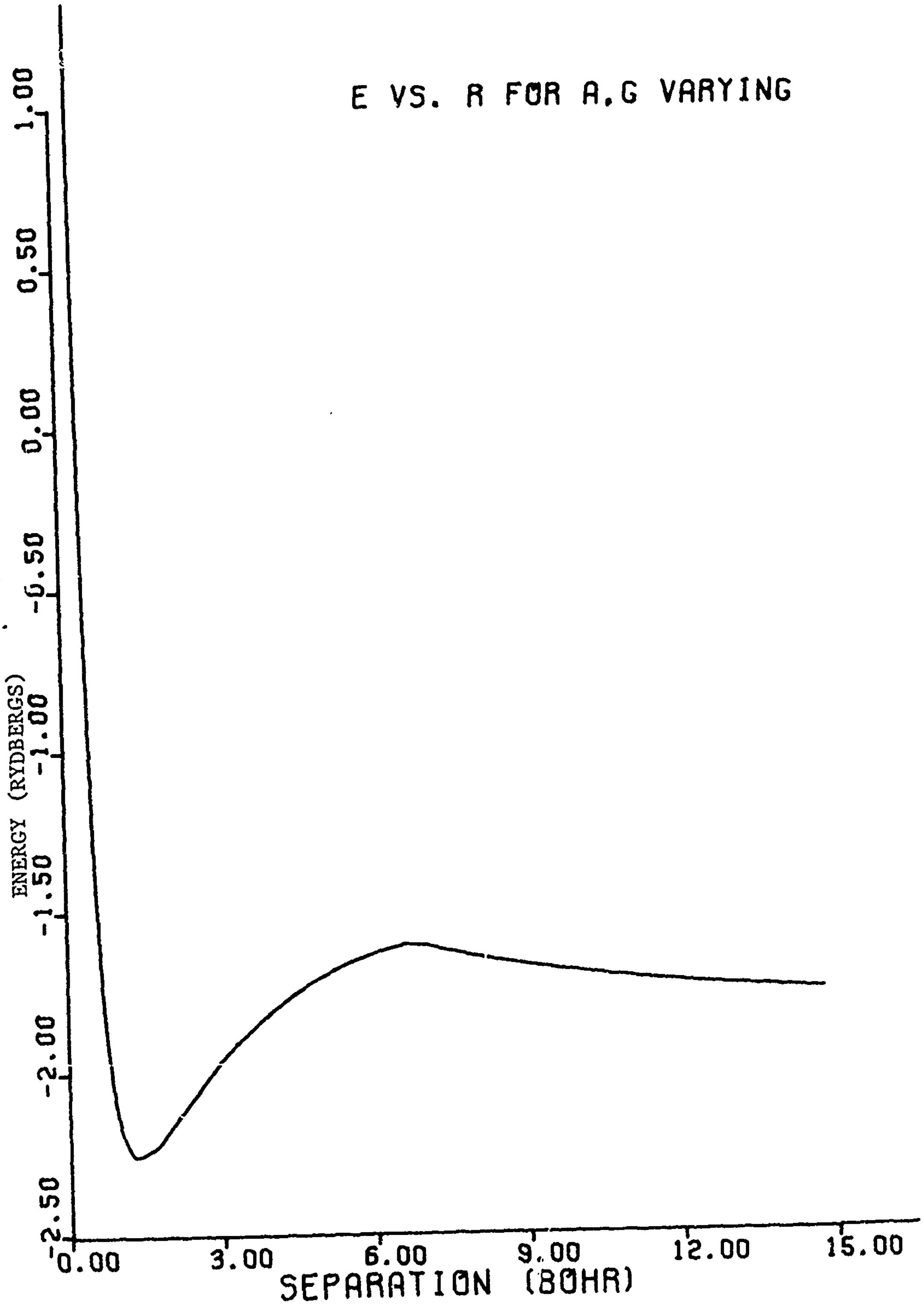


Fig. 14. Ground state energy for the doubly negative hydrogen molecular ion with variable screening.

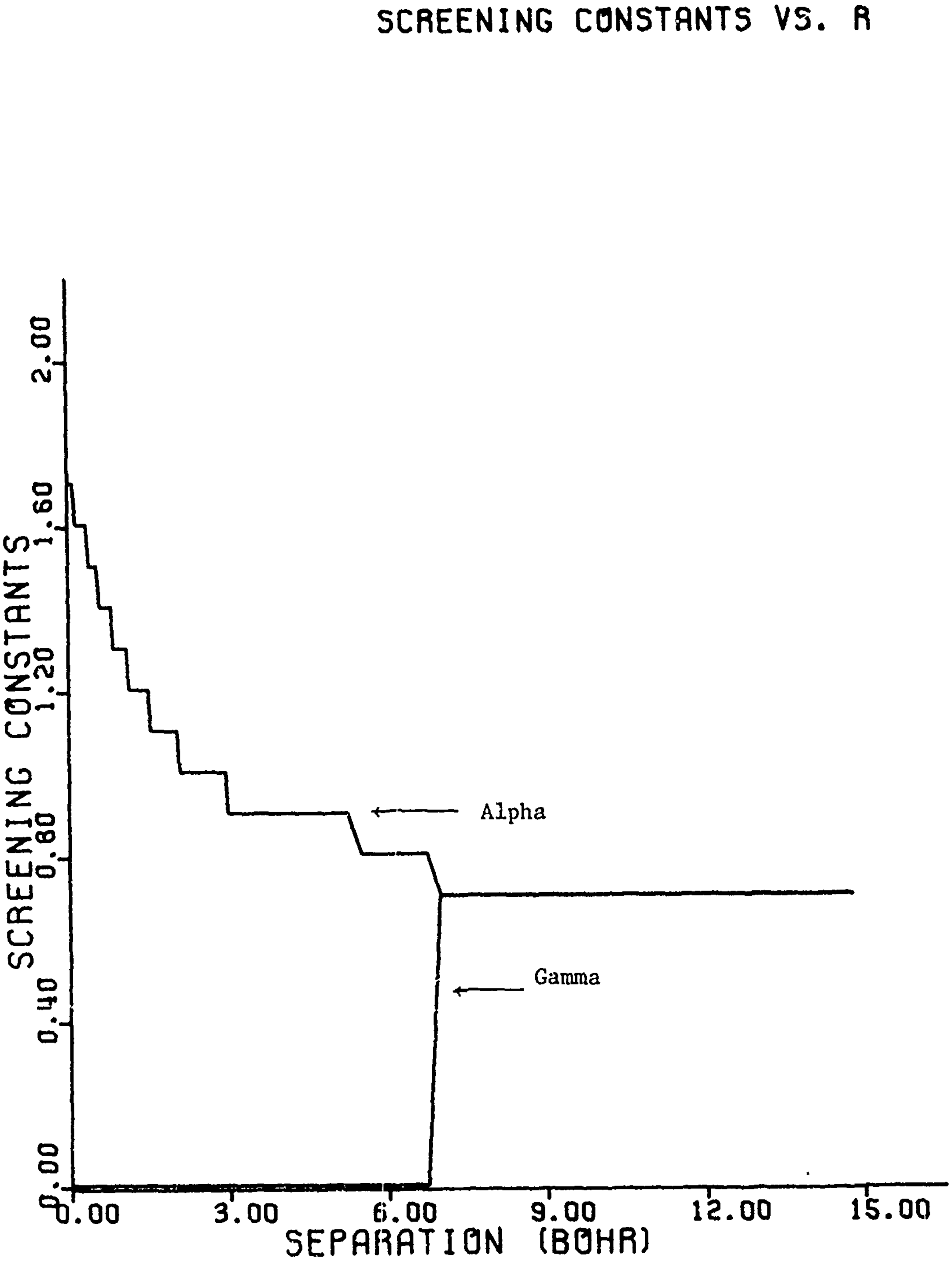


Fig. 15. Screening parameters vs. internuclear separation for the doubly negative hydrogen molecular ion ground state.

constant. In Case I (H_2), only one screening parameter was required and it was made a function of R. In case IV (H_2^{-2}), two screening parameters were used, each a function of R. The second screening constant, gamma, in Case IV is the same as alpha for R greater than 7 Bohr, but gamma drops abruptly to zero, (or, rather, to its minimum allowed value) for smaller values of the internuclear separation. This implies that the second electron is no longer bound to the system, as the screening constant may be interpreted as ($1/r_e$), where r_e is the separation between the electron and the nucleus to which it is attracted at which the radial portion of the molecular orbital wavefunction has fallen to (1/e) of its maximum value. Thus the minimum of Fig. 14 is actually the minimum for the neutral hydrogen, and is not the value which the doubly negative molecular ion would have at an equivalent separation (that is best approximated by the curve of Fig. 13). Thus what the energy function is actually doing is properly portrayed by Fig. 16, where a transition has occurred between the doubly negative ion and the neutral hydrogen at an internuclear separation of about 7 Bohr. This transition occurs by the ejection of two electrons from the system, resulting in a new system consisting of the neutral molecule plus two free electrons. The very considerable energy difference between the two curves in the region of the minimum of the neutral curve indicates the lack of stability of the molecular ion. Although the approximations inherent in the choice of the wavefunction do not allow the exact position of this transition to be determined, its existence and approximate location must be close to the indicated 7 Bohr. The magnitude of the difference

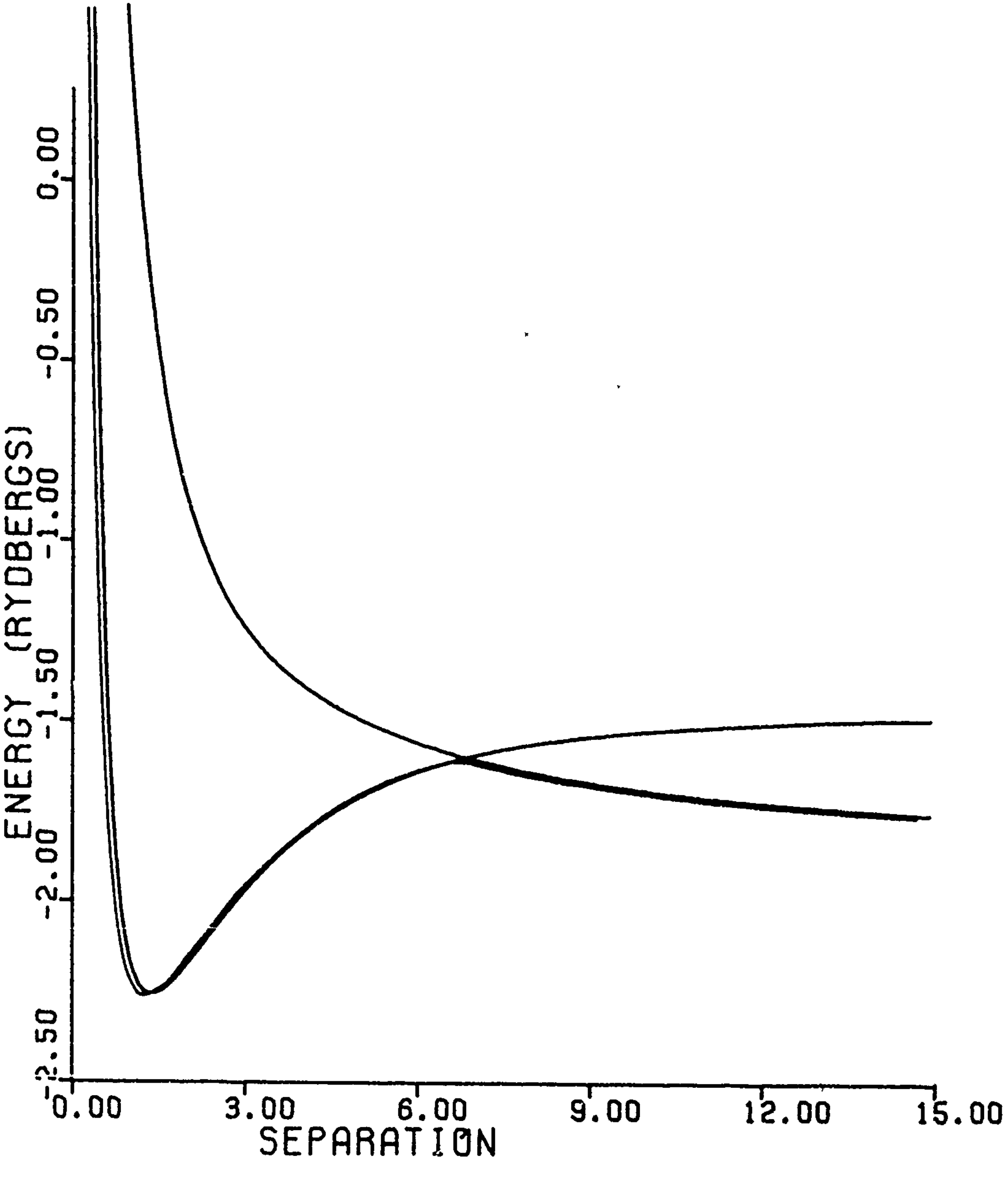


Fig. 16. Superimposed ground state energies.

between the two curves at the position of the neutral hydrogen minimum is believed to be correct.

The above may be interpreted in terms of hydride ions which approach each other from infinity. When their internuclear repulsion becomes sufficient to remove the extra electrons, allowing the formation of the neutral molecule from the molecular ion. In constructing Fig. 16, the curve of the energy using variable screening has been shifted slightly with respect to the axes to make it stand out more clearly from the other two courve, so that it does not directly overlay either of these lines. It is readily seen that this curve first follows the curve of Fig. 13 and then crosses over, following the curve of Fig. 11 at about 7 Bohr. There appears to be a small transition region near the crossover in which the energy determined for the curve allowing variation in the screening parameters is somewhat below either of the other two curves.

This calculation, on the basis of the initial wavefunction choice, does not treat the additional electrons on the hydride separately. It is therefore impossible in this calculational scheme for only a single electron to be ejected from the system. However, the values obtained by Fischer-Hjalmars (48) for the ground state energy of the H_2^{-1} system would seem to indicate that the singly negative ion ground state energy is near that of the neutral hydrogen, but probably somewhat greater (i.e., less strongly bound). It is thus probable that the results indicated above would have occurred had the calculation allowed the possibility of the ejection of electrons singly. However, in that case there might have been an additional transition region.

Case V. Neutral He_2 Molecular Calculations

As an additional check on the accuracy of the terms used in this calculation, a calculation was also made of the ground state energy of the He_2 molecule (or, if one prefers, the interaction between two He atoms). The calculation is identical in principle to the one presented by Huzinaga (49), so that the values of the terms obtained here may be checked directly with those given in his paper. A comparison of the values obtained for this calculation and by Huzinaga are given in Appendix D. The total energy for the He system is shown in Fig. 18, while the electronic terms only are shown in Fig. 17. The values of the screening constants alpha and gamma are shown as a function of internuclear separation in Fig. 19. As the values used by Huzinaga are tabulated values, his results are limited in the scope of variations of the screening constants, so that the results obtained here are somewhat more accurate for these constants. The difference of about 2 % between the values obtained by Huzinaga and those obtained by this calculation for the energy at an internuclear separation of 1 Bohr are almost entirely due to differences in the value for the K_{gu5} term where a series of approximations are necessary in order to obtain a "closed form" function of the screening constants suitable for performing the variation of parameters. To obtain a more accurate energy curve for this system, it would be possible to correct this term at selected points by a numerical integration using the values of the screening constant obtained from the approach used here. The additional accuracy would be significant only for small internuclear separations, as this term

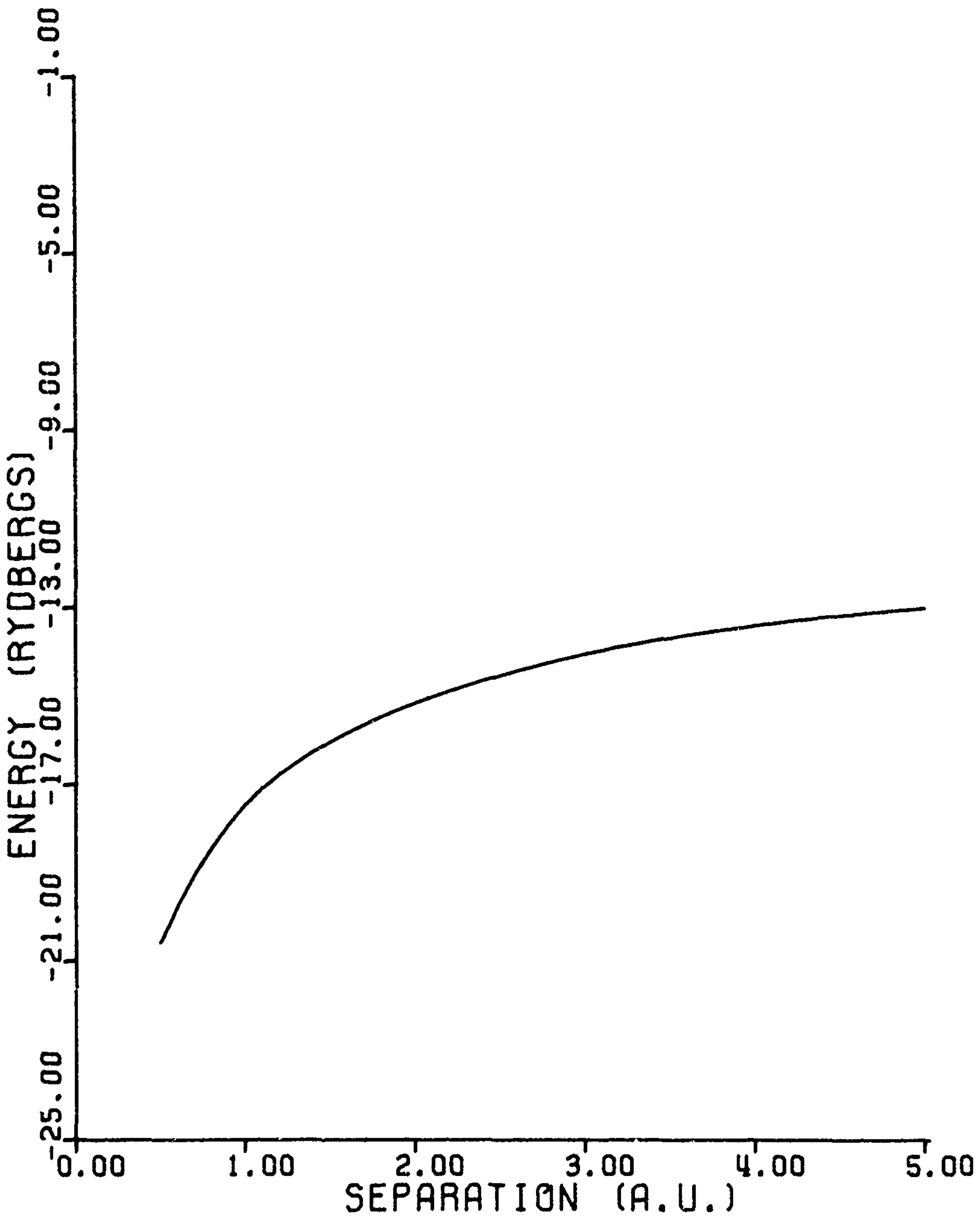


Fig. 17. Electronic ground state energy for He-He system.

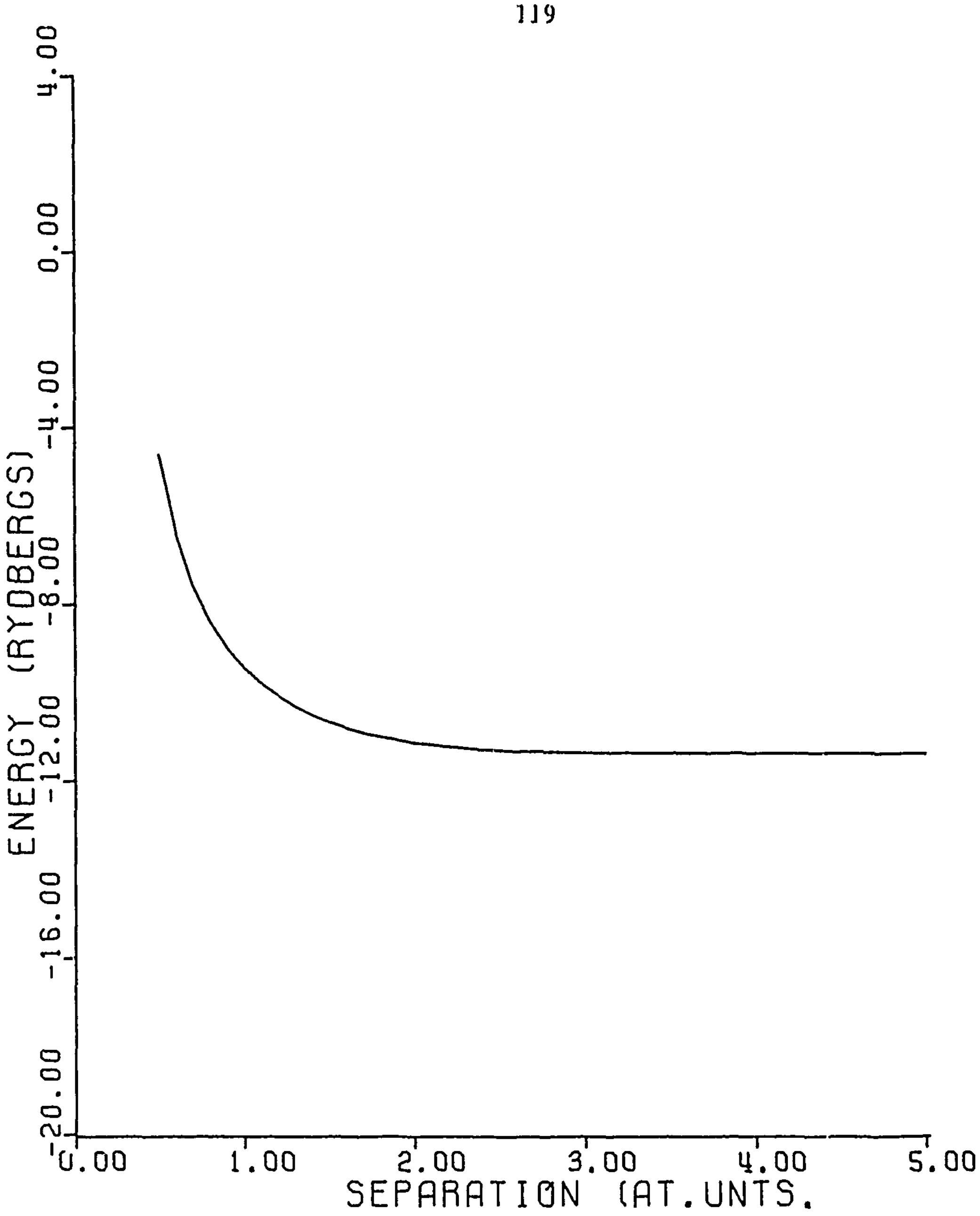


Fig. 18. Total ground state energy for He-He system.

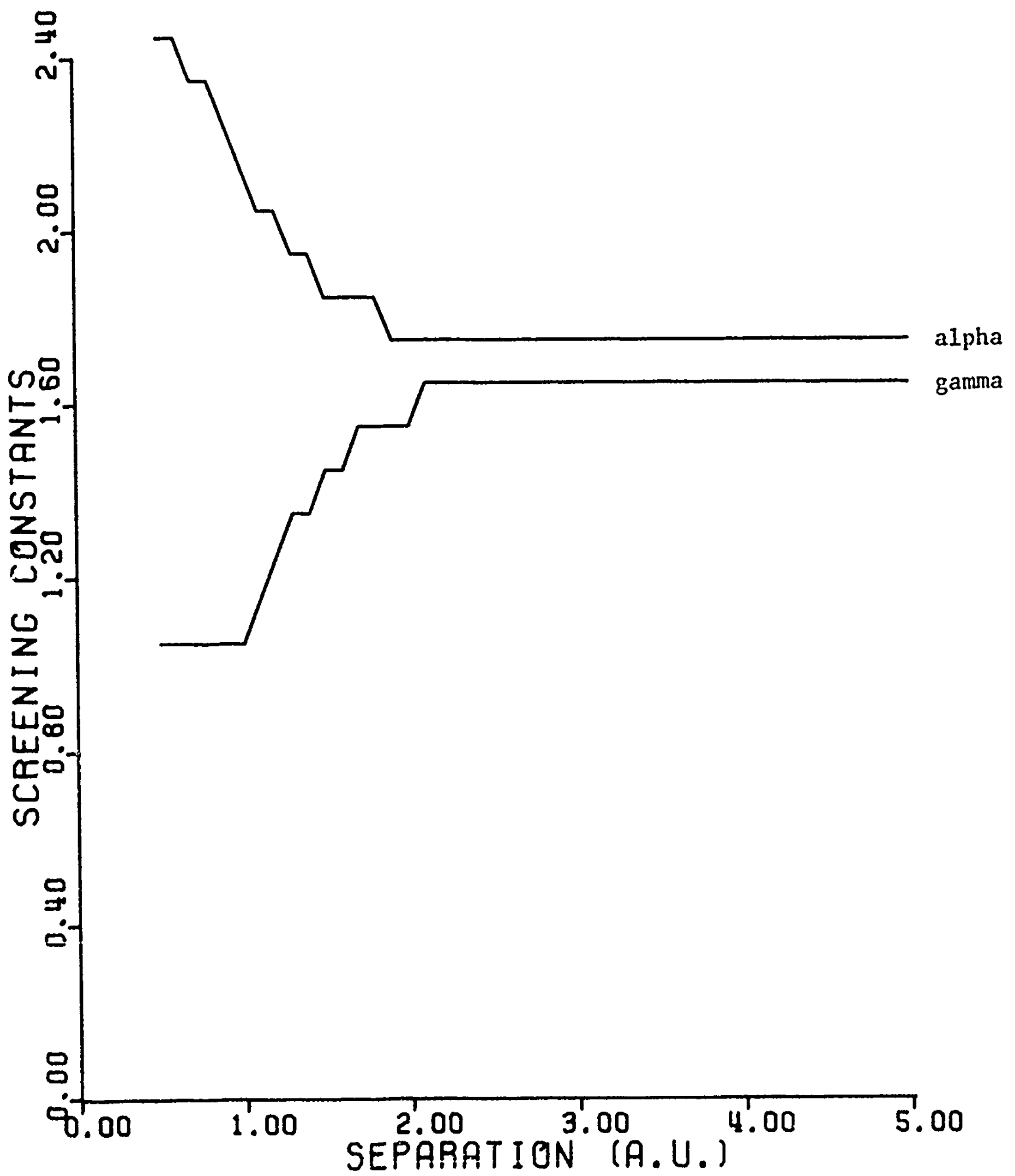


Fig. 19. Screening constants vs. internuclear separation for He-He.

drops off rapidly with increasing separation. Figures 17, 18, and 19 serve to demonstrate the essential accuracy of the individual terms used in the evaluation of the molecular ion ground state energy, and to give limits on the accuracy of the calculation.

V. DISCUSSION

If space charge in an insulator plays an important role in dielectric breakdown by causing the growth of a highly dense, highly energetic gas in the solid, there remains the necessity of explaining the manner in which the energy of the space charge is concentrated into a sufficiently small volume of the dielectric to allow the start of channel formation. Two points must be considered: firstly, the space charge distribution prior to formation of a gas, and, secondly, the space charge distribution during the actual channel formation, after the process has been initiated. Since defects serve as trapping sites, the generation and movement of defects requires further analysis.

A. Effects of Charge Imbalance on Breakdown

1. Initial Charge Distribution

There are several lines of investigation which suggest the importance of an initial imbalance of the charge distribution. The effect noted by Budenstein and Hayes (3,17) in investigations of breakdown sites by visual observation with an electron microscope is perhaps the most directly suggestive of this importance. When the capacitor under investigation was illuminated in the region of a "likely" site for the occurrence of breakdown, the breakdown event would always occur at this site. If some other region of the capacitor, not containing any such site, was illuminated, the breakdown <u>never</u> occurred in the illuminated region. The beam of the electron microscope was therefore insufficient to cause breakdown, but the extra imbalance in the charge was sufficient to determine the breakdown site. Studies of dielectric materials with much higher intensity high energy electron beams (23,24) show the patterns of breakdown characteristic of electrical breakdown in the region of penetration of the beam. In the beam experiments, an additional effect is noted in polycrystalline samples---the breakdown will frequently occur along or in the vicinity of grain boundaries.

Also of relevance in this connection are high energy beam studies in plastic dielectrics. In such cases, when a beam (several MeV) illuminates the plane surface of a plastic disk-shaped specimen, breakdown ultimately occurs with the breakdown channel originating on the illuminated surface. The observed channel goes directly to the space charge layer, then runs, with branching, along this layer and parallel to the surface (11). Localization of the breakdown channel in a plane, perpendicular to the electric field, that contains a high space charge density is strongly indicative of the importance of space charge in the breakdown process.

The mechanism for space charge build-up under application of an external electric field is frequently assumed to involve carrier injection in regions where there is a geometrical enhancement of the applied field due to asperitics. Thus for example Smith (10) assumes a hemispherical electrode projection causes a field strength of three times that of the region near the smooth portion of the electrode. Ridley (45), using a more complex geometry, shows that Smith's results yield a lower limit to the enhancement of the field, a more pointed projection giving values substantially higher. If the injection mechanism is Fowler-Nordheim emission, then the (local) injected current density is a very strong function of the electric field in the vicinity of the injecting point:

$$J = J\ (\ E^2\ \exp(-k/E)\ )$$

where only the dependence of the current density on the electric field is indicated. Thus only a small increase in the electric field can give rise to a very large change in the injected electron density. If the injected charges are trapped, then the cathode field is weakened. However, if the field continues to rise, a point will be reached when traps are filled. Subsequent injected electrons will then be accelerated for long distances and be able to acquire the energy necessary for creating ionization and defect centers, such as the V_k center.

Point defects have mobility and will move in response to a concentration gradient by diffusion. Mechanical stress, the presence of dislocations, grain boundaries, and other point defects will influence the rate of diffusion. If the defect contains an unbalanced charge or a dipole moment, then it will be influenced by the presence of the electric field or its gradient, respectively.

Dislocations and grain boundaries are regions of major misfit. Such regions tend to trap defects, thus immobilizing them. Cooper (19) has shown that carefully annealed single crystals of alkali halide exhibit about one third of the scatter in breakdown field strengths compared to similar unannealed specimens. Annealing does not appreciably alter the centroid of the distribution. If unannealed crystals tend to concentrate charged defects, then a lower breakdown strength is anticipated. If, on the other hand, the built-in imperfections strongly inhibit motion of defects, then the defect mobility is decreased and it is more difficult to reach the critical charge density requisite to start the growth of a gaseous channel. This explains how defects in unannealed crystals broadened the range of breakdown voltages without appreciably altering the mean breakdown strength.

Cooper (20) has also shown that the breakdown channels of carefully annealed single crystals tend to follow certain crystallographic directions, even when the field is 45 degrees from these directions. In unannealed crystals, the channels follow the field directions. If mobile charged defect centers, such as V_k centers, are generated continuously at a site and if these migrate more easily along the favored crystallographic directions (as is known for H centers), then a "spike" of V_k centers is produced along this direction. If the density of charge reached the critical value, then conversion of the dielectric to the gas would occur along the spike and the resulting channel would be along the favored crystallographic direction.

2. Space Charge Distribution After Channel Initiation

Following the initiation of a gas pocket, the charge distribution will alter considerably from that prior to the formation of the first gas pocket. If the assumption is made that the channel will form in the region of highest initial charge density imbalance, then one expects that the region containing the pointed electrode projection will be the point of initiation of the channel. Previously, the dominant process for removing the defect centers from the region has been diffusion. Once a gas pocket has formed, the effect of the internal field inhomogenieties within the dielectric will begin to have a more marked effect on the distribution. As was shown in Chapter III, after a gas pocket has formed, there will be forces on the centers tending to concentrate them in the region of the gas pocket. This will lead to a lessening of the net diffusion from the region, and may lead to a reversal of diffusion, as the defects are now incorporated within the gas pocket. Further, the gas pocket will offer a lower resistance to the passage of current, thereby leading to further enhancement of injection from the electrodes in this region. The greater density of current in this region, and the immediately surrounding solid dielectric, will lead to an enhancement in the production of centers. The additional centers will be placed in the dielectric in a manner leading to their rapid incorporation within the gas pocket, leading to its growth. In addition, the greater current injection entering the pocket will traverse the gas, and will perforce have to leave the pocket through largely undisturbed dielectric material. This will lead to the creation of further centers within the solid along a line determined largely by the field orientation and by the orientation of the gas pocket relative to the material. The combination of these two effects, then, serve to establish the defect density in the region where it is most likely to lead to further growth of the gas pocket.

If the gas pocket leads to a higher rate of creation of centers in this fashion by acting as a "new" cathode (as is suggested by

Lopez (56)), then one might expect there to be another such pocket formed further into the dielectric, spaced, relative to the first gas pocket, much as the first gas pocket is spaced from the cathode. In such a situation, both pockets would then repeat the process, etc. Throughout this time, each gas pocket would be growing as it is formed, increasing its volume both through the direct process of incorporating defect centers directly into the gas, and by, it may be assumed, a process of heating at the walls making use of the energy liberated on the incorporation of the defect centers. Such a process would be likely to give rise to a channel having a "beaded" appearance, such as is actually observed in some breakdowns.

The presence of extensive defects, such as slip planes, where defects may have been concentrated during the initial charge build-up stages of the process, will also have a considerable effect on the form and direction of the channel within the dielectric. Such planes, in single crystals, are normally oriented along certain directions of the dielectric. This may lead to a preferred direction of the breakdown channel in such an orientation as to incorporate the maximum available charge within the channel. The exact direction, however, has not as yet been determined to give rise to this condition. The existence of such extended defect trapping sites in polycrystalline samples would thus depend on their orientation with respect to the field.

B. Relevance of Molecular Results to Breakdown

The gaseous breakdown model requires a solid to become energetically unstable at sufficiently high charge densities. External excitation must produce intermediate states within the solid which can decay into a molecular gas. If the H_2, H_2^{-1}, and H_2^{-2} molecules are taken as prototypes for molecular bonds with different numbers of extra electrons, some general conculsions can be drawn from the calculations on the ground state energies of the hydrogen negative ion sequence.

The bonding energy in the ground state of the neutral hydrogen moleucle at its equilibrium internuclear separation of 1.4 Bohr is 0.347 Rydbergs (51), or about 4.7 eV. Fischer-Hjalmars (48) has calculated the ground state energy for the H_2^{-1} ion, obtaining a dissociation energy of 2.54 eV at its equilibrium separation of 1.65 Bohr. The minimum of the H_2^{-1} ion curve lies above that of the H_2 by 1.9 eV, with the remainder of the difference in bonding energies being due to the stability of the hydride (H^-) ion. The H_2^{-1}, then, represents a possible intermediate state, analogous to the Cl_2^- state discussed in Chapter III.

The results for H_2^{-2} show, for the case in which the screening parameters are held fixed, an energy at the position of the neutral minimum of about -0.75 Rydbergs, or about 21 eV above the neutral minimum. The state is highly repulsive, and could not form during breakdown except as a short-lived resonant state, as it lies far into the continuum range of states for neutral hydrogen. The repulsive character of the state is sufficiently pronounced that the interaction of an additional electron with the H_2^{-1} ion may cause detachment of the excess electron in the negative ion, yielding a neutral molecule plus a free electron. If the additional electron interacts elastically, then the freed electron would have an energy up to 1.9 eV. The action of the calculated ground state energy of H_2^{-2} with a variation of screening parameters also supports this conclusion. The calculations indicate the doubly negative ion changes into an H_2^0 molecule plus free electrons at an internuclear separation of 7 Bohr. Thus the H_2^{-2} state becomes energetically unfavorable at large internuclear separations. The value of the internuclear separation for the conversion gives an approximate scale of interaction ranges for the interaction of a free electron with the singly negative hydrogen ion, as the extra electron would have to be accomodated within the bonding system of the H_2^{-1} ion. This implies that the interaction would create an intermediate state during the interaction of H_2^{-2}, and so gives a range for the interaction. It is not possible from the calculations presented here to obtain significant energy information from the state energy of the H_2^{-2} ion obtained by the variation of parameters, due to the ionization of the extra electrons from the ion and consequent conversion into neutral hydrogen, as discussed in Chapter IV.

From the progression of ground state energies, it can be seen that a sufficient number of excess electrons introduced into the bonding system will lead to the disruption of molecular bonding. This is shown in Table 5, where the ground state energies are given relative to a zero energy for separated nuclei and electrons at infinity. The introduction of two electrons into the bonding system in addition to those

TABLE 5

GROUND STATE ENERGIES AND EQUILIBRIUM INTERNUCLEAR SEPARATIONS FOR THE HYDROGEN NEUTRAL AND NEGATIVE ION MOLECULAR ION SEQUENCE

SPECIES	GROUND STATE ENERGY (Rydbergs)	EQUILIBRIUM SEPARATION (Bohr)
H_2^{o}	-2.73	1.40
H_2^{-1}	-2.21	1.65
H_2^{-2}	-0.75	none

normally present in the neutral is sufficient to disrupt totally the bonding. In the case of excited states, Taylor et al (57) have shown that the singly negative ion possesses no bound excited states; this is also obviously true with regards to the doubly negative system.

The energies associated with bonds in condensed matter vary from a few tenths of electron volts to several electron volts. If the binding energies of the H_2^{o}, H_2^{-1}, and H_2^{-2} systems are taken as representative of other molecular charge-variable systems, a perspective is provided for the proposed gaseous breakdown mechanism. The addition of an extra electron to a single bonding pair decreases the bond stability by about 2 eV with only a small relaxation of the internuclear separation. An additional electron makes the system strongly unstable. Instability arises, then, for an excess charge of between one and two extra electrons. The case considered in the detailed analysis was that of an isolated molecule. In condensed matter, molecular bonds between two adjacent atoms are not completely independent of those of surrounding atoms. If excess electrons are added in low concentrations in a solid insulator, they generally become trapped. In so doing, they modify the local energy level structure. Each such electron will contribute to the electrical potential energy of a-1 atoms containing trapped electrons. If the trap density becomes high enough, then the perturbing potential would reach the condition where nonbonding orbitals are produced. (In the sense used here, the term nonbonding includes both nonbonding and antibonding orbitals.) This condition is exemplified by the lack of stability of the H_2^{-2} molecular ion.

An estimate of the charge density necessary for the production of nonbonding orbitals may be obtained from breakdown experiments on electron-beam irradiated plastic specimens. If a thick slab is irradiated by a beam having an energy of several MeV, the breakdown occurs when the field due to the trapped charges is 10^6-10^7 V/cm, and the discharge path goes from the upper surface down to the charge layer and through this layer (parallel to the surface and almost perpendicular to the field direction) to the lateral surfaces. A field of 10^6-10^7 V/cm implies a charge layer of 10^{12} or 10^{13} electrons/cm^2. If this charge is concentrated in a layer 1 micron thick, the average distance between defect centers is about 200 Å.

Tang et al (58) have studied the increase in electrical conductivity with applied field in silver azide (AgN_3) and explained their results in terms of formation of an intermediate N_3^- molecular state. Their experimental arrangement involves the study of a single crystal of silver azide with applied fields of up to 3.5 KV/cm under high vacuum conditions. Electrode contact-related phenomena were also studied in their experiments, and mass-spectrographic analysis was carried out on the reaction products and evolved gas during the reactions. Decomposition of the crystal was detected with applied fields as low as 0.3 KV/cm, although the decomposition rate varied widely between samples. For sinusoidally time varying fields, decomposition was not observed to occur for frequencies above 15 Hertz and fields up to 1.7 KV/cm (peak to peak). When only one contact was made between the electrodes and the crystal, decomposition occurred only when that electrode was the cathode. The decomposition product monitored was molecular nitrogen;

in some samples, "bursts" of nitrogen were detected superimposed on a general background level. The decomposition reaction proceeds through the formation of an intermediate N_3^-, having an energy of about 2 eV above the ground state of the system. In all the azides, the breakdown will proceed slowly at lower field strengths than those necessary for channel formation and other features normally associated with breakdown.

Capacitors subjected to high field strengths over long periods of time show aging effects, including reduced breakdown field strengths. Aging may be due to intermediate states formed over a period of time at field strengths less than those required for breakdown. Deterioration would be associated with formation of a gas molecule rather than a return to the original stable lattice. This effect would thus lead to regions in which the dielectric is less stable than the original material; such centers might serve also as nucleation centers for additional intermediate states once they are formed. This would thus link the phenomenon of aging in dielectrics directly to the breakdown, with the primary difference being largely one of time scale.

C. Summary

Dielectric breakdown, according to the model proposed by Budenstein, involves the growth of a localized conducting gaseous channel through the dielectric under the action of an external electric field. In this study, two questions relevant to the early stages of the solid-to-gas conversion have been addressed and placed in improved perspective:

(1) How is energy added to the solid so that the solid-to-gas conversion can occur? (2) What is the mechanism for the solid-to-gas conversion?

The first question has been explained by showing that point defects can be introduced that have excess energies. The energy of formation of these defects comes from the external electric field; electrons in the conduction band of the insulator are assumed to be accelerated to sufficiently high energies (several eV) that they can produce collisional ioziation and, thereby, point defects. The number of defect centers required for creation of a gaseous breakdown channel is about the same as the number of atoms of the solid that are converted to gas in this channel.

The second question, on the nature of the mechanism of solid-to-gas conversion, has been answered by hypothesizing the creation of nonbonding orbitals when the local excess charge density is increased sufficiently. To obtain quantitative information on the role of excess charge density on molecular bonding, the bonding characteristics of the molecular sequence H_2^o, H_2^{-1}, and H_2^{-2} was studied. This required ab initio calculation of the H_2^{-2} molecular ion. Both H_2^o and H_2^{-1} have stable ground state configurations, while the H_2^{-2} is strongly repulsive for all internuclear separations. The results of the molecular calculations were applied qualitatively to bonding within a solid. By taking the field due to space charge to be of the same order of magnitude as the breakdown field, it was estimated that an excess of one electron exists for about every 10^6 atoms in the breakdown location. For the rapid conversion of solid to gas, an energy of several electron volts per atom is required. Defect centers have energies of formation in this range. Trapped electrons in the vicinity of defect centers will alter the energy level structure at the defect. Nonbonding orbitals are assumed to arise when the trapped electrons interact strongly enough with the defect center. This is the sought after conversion of solid to gas.

Features of breakdown in solids that have been placed in improved perspective by the above considerations include the following.

1. The formative period after the initiation of voltage stress is here associated with the need to store energy in the solid so that the solid-to-gas transformation can occur.
2. The formative period is here related to the generation of point defects due to collisonal ionization.
3. Point defects should form more readily in regions already partially disordered and in regions of high field. The electric field may be locally enhanced through geometric irregularities and space charge effects.
4. The evolution of nonbonding orbitals has been followed for a particular molecular system: H_2 with zero, one, and two extra electrons. The latter case has been evaluated for different internuclear separations, including those of the H_2^{o} and H_2^{-1} molecules. The ideas of this evolution have been applied to the creation of nonbonding orbitals in solids due to trapped charges about defect centers. This is taken as the mechanism for converting atoms of the solid to atoms of a gas.

5. Point defects can serve as a source of prebreakdown recombination radiation.

6. The radius of a trapped electron is greater if the dielectric has a high dielectric constant. Hence, a lower density of electrons is needed to alter significantly the energy levels at defect sites. Thus, nonbonding energy levels will arise at a lower applied field and the solid-to-gas conversion will be initiated at a lower field. Dielectric breakdown will occur at lower fields for materials with higher dielectric constants.

7. A material that is disordered has a wider spectrum of trapping levels than a material that is more ordered. Deep traps will yield more localization of the trapped charges than shallow traps. The detailed trap distribution will play an important role on the breakdown threshold. This distribution will be influenced by a-nealing.

8. Defects can form at lower than breakdown fields, as can space charge due to electrons. Thus molecular bonds can be broken in a limited region. This constitutes aging of the dielectric. The rate-limiting process in the aging is probably the creation of the defect centers. Thus chemical effects, absorption of moisture, diffusion of active gases and similar perturbations can provide the energy for the defect centers.

D. Suggestions for Future Work

The present work has increased the credibility of the gaseous model of electric breakdown in solids, but much work remains before the model can be accepted without reservation. Tasks to be done include the following.

1. Quantitative investigation of point defect formation through collisional ionizaiton and other mechanisms. Analysis of stability and mobility of defects in high uniform and nonuniform electric fields
2. Quantitative investigation of the role of space charge on the energy level structure of defect centers and the creation of nonbonding states.
3. Dynamics of growth of the gaseous channel prior to the completion of the channel.
4. Growth dynamics of the gaseous channel after completion of the gaseous bridge between electrodes.
5. Application of the ideas of defect formation and bond breakage to low fields and long times to explain aging effects.

REFERENCES

1. J. J. O'Dwyer, The Theory of Electrical Conduction and Breakdown in Solid Dielectrics. Clarendon Press, Oxford (1973)
2. R. Cooper, Brit. J. Appl. Phys. 17, 149 (1966)
3. P. P. Budenstein and P. J. Hayes, J. Appl. Phys. 38, 2837 (1967)
4. P. P. Budenstein and J. Lloyd, Conf. Elec. Insul. Diel. Phenom. (1975)(National Academy of Sciences, Washington, D.C.)
5. B. K. Ridley, J. Appl. Phys. 46, 998 (1975)
6. T. H. DiStefano and M. Shatzkes, J. Vac. Sci. Technol. 12, 37 (1975)
7. S. Whitehead, Dielectric Breakdown in Solids, Clarendon Press, Oxford (1951)
8. N. Klein, "Electrical Breakdown in Solids," Adv. Electronics and Electron Phys. 26, 309 (1967)
9. R. Cooper, "The Electrical Strength of Solid Dielectrics," Brit. J. Appl. Phys. 17, 149 (1966)
10. W. Smith, M. S. Thesis, Auburn University (1969)
11. P. P. Budenstein, in Digest of Literature on Dielectrics, Ed. W. E. Vaughn, National Acad. Sciences, Washington, D.C. (1973)
12. P. P. Budenstein, REPORT RG-75-25 (1974)
13. I. Adamacewski, Ionization, Conductivity, and Breakdown in Dielectric Liquids. Taylor and Francis, London (1969)
14. P. Hayes, M. S. Thesis, Auburn University (1966)
15. J. L. Smith, Ph. D. Dissertation, Auburn University (1968)
16. D. B. Watson and W. Heyes, J. Phys. Chem. Solids 31, 2531 (1970)
17. P. P. Budenstein, Final Report, NASA Grant NGR-01-003-011 (1968)

18. G. A. Vorob'ev and M. N. Lisetskaya, Sov. Phys. Tech. Phys. 11, 1405 (1967)(English)

19. R. Cooper and C. T. Elliott, J. Phys. D1, 121 (1968)

20. R. Cooper and D. L. Pulfrey, J. Phys. D4, 292 (1971)

21. A. Grinberg and D. M. K. deGrinberg, J. Appl. Phys. 45, 2007 (1974)

22. R. Cooper, Private Communication (1976)

23. Z. Morlin and J. Tremel, Czech. J. Phys. 13, 216 (1963)(English)

24. M. Creutzburg, Z. Physik 194, 211 (1966)(German)

25. N. Tsuchida and M. Ueda, Conf. Elect. Insul. Diel. Phenom. page 200 (1973)

26. W. Franz, "Dielektrischer Durchschlug," Handbuch der Physik, V 17, Springer Verlag (1956)(German)

27. A. von Hipple, Ergebn. Exakt. Naturw. 14, 79 (1935)(German)

28. H. B. Callen, Phys. Rev. 76, 1394 (1949)

29. C. Zener, Proc. Royal Soc. A160, 230 (1934)

30. W. Franz, Z. Physik 113, 607 (1939)(German)

31. J. J. O'Dwyer, J. Phys. Chem. Solids 28, 1137 (1967)

32. J. J. O'Dwyer, J. Electrochem. Soc. 116, 239 (1969)

33. J. J. O'Dwyer, Conf. Elect. Insul. Diel. Phenom. (1969)

34. B. K. Ridley, J. Appl. Phys. 46, 998 (1975)

35. P. P. Budenstein, Contract Report DAHC04-72-0001 (1973)

36. C. Paracchini, Phys. Rev. B4, 2342 (1971)

37. J. G. Simmons "Electronic Conduction through Thin Insulating Films" in Handbook of Thin Film Technology, Ed. Maissel, L. I. and R. Glang, McGraw-Hill, New York (1970)

38. G. J. Dienes, Report BNL-50336, page 214 (1974)

39. W. B. Fowler, Physics of Color Centers, Academic Press, New York (1968)

40. P. D. Townsend and J. C. Kelly, Colour Centers and Imperfections in Insulators. Crane, Russak, New York (1973)

41. J. H. Schulman and W. D. Compton, Color Centers in Solids, Pergamon Press, Oxford (1962)

42. C. Paracchini, Lumin. Cryst. Mol., Solutions, Proc. Intl. Conf. (1972)

43. D. Pooley, Proc. Phys. Soc. 87, 245 (1966)

44. Handbook of Chemistry and Physics, 54th Ed. Chemical Rubber Press (1973)

45. G. W. Thompson and E. Garelis, Sodium—Its Manufacture, Properties and Uses, Ed. M. Sittig, Ch. 3 Reinhold Publishing Co., New York (1956)

46. R. Cooper, Private Communication (1976)

47. C. F. Conf. Elect. Insul. Diel. Phenom, page 472, National Academy of Sciences, Washington, D.C. (1974)

48. I. Fischer-Hjalmars, Arkiv. f. Fysik 16, 33 (1959)(English)

49. S. Huzinaga, Prof. Theor. Phys. 18, 139 (1959)

50. M. Abramowitz and I. Stegun, Eds., Handbook of Mathematical Functions. U. S. National Bureau of Standards, Washington, D.C. (1965)

51. J. C. Slater, Quantum Theory of Molecules and Solids, Vol. I. McGraw-Hill, New York (1963)

52. S. Weinbaum, J. Chem. Phys. 1, 593 (1933)

53. S. C. Wang, Phys. Rev. 31, 579 (1928)

54. N. Rosen, Phys. Rev. 38, 2099 (1931)

55. S. Chandresakhar, Astrophys. J. 100, 176 (1944)

56. C. Sanchez-Lopez, Mem. R. Acad. Cienc. Exactas, Fis. Nat. Madrid, Ser. Cien. Fis-Quim 7, 68 (1974)(Abstract only-C.A. 82-179581)

57. I. Eliezer, H. S. Taylor, and J. K. Williams, J. Chem. Phys. 47, 2165 (1967)

58. T. B. Tang, R. G. Patel, and M. M. Chaudri. "Some Studies of Breakdown in Metal Azides," Preprint, Conf. Elect. Insul. Diel. Phenom, (1976)

59. Y. Farge, J. de Physique (Paris) Colloque 9, 475 (1973)(English)

60. P. A. Kask. R. A. Kink, G. G. Liidya, T. A. Soovik, Opt. Spektrosk 37, 942 (1974)(English)

61. A. N. Jette, T. L. Gilbert, T. P. Das, Phys. Rev. 184, 884 (1969)

62. T. L. Gilbert and A. C. Wahl, J. Chem. Phys. 55, 5247 (1971)

63. R. Balzer, H. Peisl, H. Peters, W. Waidelich, J. de Physique Colloque 9, 34 (1973)(English)

64. M. J. Norgett and A. M. Stoneham, J. Phys. C: Solid State Physics 6, 229 (1973)

65. A. M. Stoneham, J. Phys. C: Solid State Physics 6, 223 (1973)

66. A. Mainwood and A. M. Stoneham, J. Phys. C: Solid State Physics 8, 3059 (1975)

67. H. F. Ivey, Electroluminescence and Related Effects. Academic Press, New York (1963)

68, A. M. Stoneham, Theory of Defects in Solids. Clarendon Press, Oxford (1975)

APPENDIX A

EXPANSION OF THE SLATER DETERMINANT AND GROUPING OF THE WAVEFUNCTION

As given in Eq. (7), the ground state wavefunction for the double negative hydrogen molecular ion is given by the (expanded) Slater determinant

$$\text{(A-1)} \quad \psi = \frac{1}{\sqrt{24}} \begin{vmatrix} \phi_g(1)\alpha(1) & \phi_g(2)\alpha(2) & \phi_g(3)\alpha(3) & \phi_g(4)\alpha(4) \\ \phi_g(1)\beta(1) & \phi_g(2)\beta(2) & \phi_g(3)\beta(3) & \phi_g(4)\beta(4) \\ \phi_u(1)\alpha(1) & \phi_u(2)\alpha(2) & \phi_u(3)\alpha(3) & \phi_u(4)\alpha(4) \\ \phi_u(1)\beta(1) & \phi_u(2)\beta(2) & \phi_u(3)\beta(3) & \phi_u(4)\beta(4) \end{vmatrix}$$

This determinant is expanded, giving the next form for the wavefunction: it will be noted that here the space and spin components of the wavefunction are now grouped separately rather than kept together. The expanded wavefunction is

$$\text{(A-2)} \quad \psi = \frac{1}{\sqrt{24}} \{\phi_g(1)\phi_g(2)\phi_u(3)\phi_u(4)\alpha(1)\beta(2)\alpha(3)\beta(4)$$

$$+ \phi_g(1)\phi_g(3)\phi_u(2)\phi_u(4)\alpha(1)\beta(2)\beta(3)\alpha(4) + \phi_g(1)\phi_g(4)\phi_u(2)\phi_u(3)\alpha(1)\alpha(2)$$

$$\beta(3)\beta(4) - \phi_g(1)\phi_g(2)\phi_u(3)\phi_u(4)\alpha(1)\beta(2)\beta(3)\alpha(4) - \phi_g(1)\phi_g(3)\phi_u(2)\phi_u(4)$$

$$\alpha(1)\alpha(2)\beta(3)\beta(4) - \phi_g(1)\phi_g(4)\phi_u(2)\phi_u(3)\alpha(1)\beta(2)\alpha(3)\beta(4) + \phi_g(1)\phi_g(2)$$

$$\phi_u(3)\phi_u(4)\beta(1)\alpha(2)\beta(3)\alpha(4) + \phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4)\alpha(1)\alpha(2)\beta(3)\beta(4) +$$

$$\phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)\beta(1)\alpha(2)\alpha(3)\beta(4) - \phi_g(1)\phi_g(2)\phi_u(3)\phi_u(4)\beta(1)\alpha(2)$$

$$\alpha(3)\beta(4) - \phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4)\beta(1)\alpha(2)\beta(3)\alpha(4) - \phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)$$

$$\alpha(1)\alpha(2)\beta(3)\beta(4) + \phi_g(1)\phi_u(2)\phi_g(3)\phi_u(4)\beta(1)\alpha(2)\alpha(3)\beta(4) + \phi_u(1)\phi_g(2)$$

$$\phi_g(3)\phi_u(4)\beta(1)\beta(2)\alpha(3)\alpha(4) + \phi_u(1)\phi_u(2)\phi_g(3)\phi_g(4)\alpha(1)\beta(2)\alpha(3)\beta(4) -$$

$$\phi_g(1)\phi_u(2)\phi_g(3)\phi_u(4)\beta(1)\beta(2)\alpha(3)\alpha(4) - \phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4)\alpha(1)\beta(2)$$

$$\alpha(3)\beta(4) - \phi_u(1)\phi_u(2)\phi_g(3)\phi_g(4)\beta(1)\alpha(2)\alpha(3)\beta(4) + \phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)$$

$$\beta(1)\beta(2)\alpha(3)\alpha(4) + \phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)\alpha(1)\beta(2)\beta(3)\alpha(4) + \phi_u(1)\phi_u(2)$$

$$\phi_g(3)\phi_g(4)\beta(1)\alpha(2)\beta(3)\alpha(4) - \phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\alpha(1)\beta(2)\beta(3)\alpha(4) -$$

$$\phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)\beta(1)\beta(2)\alpha(3)\alpha(4) - \phi_u(1)\phi_u(2)\phi_g(3)\phi_g(4)\alpha(1)\beta(2)$$

$$\beta(3)\alpha(4)\}$$

The space-portions of the wavefunction, $\phi_g(n)$ and $\phi_u(n)$ for the nth electron are defined by Eqs. (1) and (3) of Chapter IV, and the spin-portion of the wavefunction is denoted by $\alpha(n)$ for spin-up and $\beta(n)$ for spin-down.

By regrouping and factoring into the (six) spin components, one obtains the form

$$
\begin{gathered}
\text{(A-3)} \quad \psi = \frac{1}{\sqrt{24}} \Big[\{\phi_g(1)\phi_g(4)\phi_u(2)\phi_u(3) - \phi_g(1)\phi_g(3)\phi_u(2)\phi_u(4) + \phi_u(1) \\
\phi_g(2)\phi_g(3)\phi_u(4) - \phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)\Big]\ \alpha(1)\alpha(2)\beta(3)\beta(4) + \Big[\phi_g(1)\phi_g(2) \\
\phi_u(3)\phi_u(4) - \phi_g(1)\phi_g(4)\phi_u(2)\phi_u(3) + \phi_u(1)\phi_u(2)\phi_g(3)\phi_g(4) - \phi_u(1)\phi_g(2) \\
\phi_g(4)\phi_u(4)\Big]\ \alpha(1)\beta(2)\alpha(3)\beta(4) + \Big[\phi_g(1)\phi_g(3)\phi_u(2)\phi_u(4) - \phi_g(1)\phi_g(2) \\
\phi_u(3)\phi_u(4) + \phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4) - \phi_u(1)\phi_u(2)\phi_g(3)\phi_g(4)\Big]\ \alpha(1)\beta(2)\beta(3) \\
\alpha(4) + \Big[\phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4) - \phi_g(1)\phi_g(2)\phi_u(3)\phi_u(4) + \phi_g(1)\phi_u(2)\phi_g(3) \\
\phi_u(4) - \phi_u(1)\phi_u(2)\phi_g(3)\phi_g(4)\Big]\ \beta(1)\alpha(2)\alpha(3)\beta(4) + \Big[\phi_g(1)\phi_g(2)\phi_u(3)\phi_u(4) \\
- \phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4) + \phi_u(1)\phi_u(2)\phi_g(3)\phi_g(4) - \phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\Big] \\
\beta(1)\alpha(2)\beta(3)\alpha(4) + \Big[\phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4) - \phi_g(1)\phi_u(2)\phi_g(3)\phi_u(4) + \phi_g(1) \\
\phi_u(2)\phi_u(3)\phi_g(4) - \phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)\Big]\ \beta(1)\beta(2)\alpha(3)\alpha(4)\}
\end{gathered}
$$

Denote each space portion by f_i and each spin portion by s_i. Then the wavefunction takes the form

$$\text{(A-4)}\quad \psi = \frac{1}{\sqrt{24}} \{f_1 s_1 + f_2 s_2 + f_3 s_3 + f_4 s_4 + f_5 s_5 + f_6 s_6\}$$

where $s_1 = \alpha(1)\alpha(2)\beta(3)\beta(4)$

$s_2 = \alpha(1)\beta(2)\alpha(3)\beta(4)$

$s_3 = \alpha(1)\beta(2)\beta(3)\alpha(4)$

$s_4 = \beta(1)\alpha(2)\alpha(3)\beta(4)$

$s_5 = \beta(1)\alpha(2)\beta(3)\alpha(4)$

$s_6 = \beta(1)\beta(2)\alpha(3)\alpha(4)$

The f_i may easily be obtained from direct comparison with the previous form, Eq. (A-3). Thus, in a more compact notation,

$$\text{(A-4.1)}\quad \psi = \frac{1}{\sqrt{24}} \sum_{i=1}^{6} f_i s_i$$

Since $\psi^* = \psi$ for this wavefunction, the ground state energy is given by

$$\text{(A-5)}\quad E = \int \psi^* H \psi dV = \frac{1}{24} \int (\sum_{i=1}^{6} f_i s_i) H (\sum_{j=1}^{6} f_j s_j) dV$$

Also,

$$\text{(A-5.1)} \qquad E = \frac{1}{24}\int \Big(\sum_{i=1}^{6}\sum_{j=1}^{6} f_i H f_j s_i s_j\Big) dV$$

since the Hamiltonian function H is spin independent. But $s_i s_j = \delta_{ij}$, so that the double summation reduces to a single sum:

$$\text{(A-5.2)} \qquad E = \frac{1}{24}\int \Big(\sum_{i=1}^{6}\sum_{j=1}^{6} f_i H f_j\Big)\delta_{ij} dV = \frac{1}{24}\int \Big(\sum_{i=1}^{6} f_i H f_i\Big) dV$$

Within the integral, the electron numbers may be permuted, as they are only dummy variables. If the order of integration and summation are interchanged, the result is obtained that

$$\text{(A-6)} \qquad E = \frac{1}{24}\sum_{i=1}^{6}\int f_i H f_i dV$$

Returning to the f_i, electron numbers may be permuted and nuclear labels a and b interchanged (as they indicate dummy variables in integrals). Thus

$$\text{(A-7)} \qquad E = \frac{1}{24}\sum_{i=1}^{6}\int f_i H f_i dV$$

or

$$E = \frac{1}{4}\int f_i H f_i dV$$

This is the result desired, and is given in the main body of the text as Eq. (9), where the Hamiltonian H has been expanded.

GROUPING OF THE ENERGY INTEGRAL

From Eq. (9),

$$\text{(A-8)}\quad E = \frac{1}{4}\{\int f_1{}^* \sum_{i=1}^{4} (-\nabla_i^2 - \frac{2}{r_{ai}} - \frac{2}{r_{bi}})\, f_i dV$$

$$+ \int f_1{}^*(\sum_{i>j=1}^{4} \frac{2}{r_{ij}})\, f_1 dV + \frac{2}{R}\int f_1{}^* f_1 dV\}$$

Consider first the last term:

$$\text{(A-9)}\quad \int f_1{}^* f_1 dV = \iiiint \Big[\phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4) - \phi_g(1)\phi_u(2)\phi_g(3)\phi_u(4)$$

$$+ \phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4) - \phi_u(1)\phi_g(2)\phi_u(3)\phi_g(4)\Big]\, dV_1 dV_2 dV_3 dV_4$$

For simplicity, denote these terms as f_{11}, f_{12}, f_{13}, and f_{14}. Then

$$\text{(A=9.1)}\quad \int f_1{}^* f_1 dV = \int f_{11}^2 dV + \int f_{12}^2 dV + \int f_{13}^2 dV + \int f_{14}^2 dV - 2\int f_{11}$$

$$f_{12} dV - 2\int f_{11} f_{14} dV - 2\int f_{12} f_{13} dV - 2\int f_{13} f_{14} dV + 2\int f_{11} f_{13} dV +$$

$$2\int f_{12} f_{14} dV$$

The integral of a diagonal term is definitely non zero: explicitly

$$\text{(A-10)}\quad \int f_{11}^2 dV = \int \Big[\phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\Big]^2 dV$$

$$= \int \phi_g(1)\phi_g(1)dV_1 \int \phi_u(2)\phi_u(2)dV_2 \int \phi_u(3)\phi_u(3)dV_3 \int \phi_g(4)\phi_g(4)dV_4$$

$$= (1)(1)(1)(1) = 1$$

and similarly for the other diagonal terms.

Of the off-diagonal terms, (choosing the first term as representative)

$$\text{(A-11)} \qquad \int f_{11}f_{12}dV = \int\left[\phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\right]\left[\phi_g(1)\phi_u(2)\phi_g(3)\phi_u(4)\right]dV$$

$$= \int \phi_g(1)\phi_g(1)dV_1 \int \phi_u(2)\phi_u(2)dV_2 \int \phi_u(3)\phi_g(3)dV_3 \int \phi_g(4)\phi_u(4)dV_4$$

Now $\displaystyle\int \phi_u(3)\phi_g(3)dV_3 = N_gN_u \int (\chi_a' - \chi_b')(\chi_a + \chi_b)dV$

$$= N_gN_u \int (e^{-\gamma r_a} - e^{-\gamma r_b})(e^{-\alpha r_a} + e^{-\alpha r_b}) \frac{\sqrt{\alpha^3\gamma^3}}{\pi}\, dV$$

$$= N_gN_u \frac{\sqrt{\alpha^3\gamma^3}}{\pi} \int (e^{-(\alpha+\gamma)r_a} - e^{-(\alpha+\gamma)r_b} - e^{-\alpha r_a}e^{-\gamma r_b} + e^{-\gamma r_a}e^{-\alpha r_b})dV$$

$$= N_gN_u \frac{\sqrt{\alpha^3\gamma^3}}{\pi} \left\{\int e^{-(\alpha+\gamma)r_a}dV - \int e^{-(\alpha+\gamma)r_b}dV - \int e^{-\alpha r_a}e^{-\gamma r_b}dV + e^{-\gamma r_a}e^{-\alpha r_b}dV\right\}$$

In the second and fourth integrals, interchange the labelling of atomic sites. Then Eq. (A-11) becomes

(A-12) $$N_g N_u \frac{\sqrt{\alpha^3\gamma^3}}{\pi} \{ \int e^{-(\alpha+\gamma) r_a} dV - \int e^{-(\alpha+\gamma) r_a} dV - \int e^{-\alpha r_a} e^{-\gamma r_b} dV + \int e^{-\gamma r_b} e^{-\alpha r_a} dV$$

and it is immediately seen that the first and second sets of integrals add to zero, pairwise.

Thus

(A-13) $$\int f_{11} f_{12} dV = 0$$

and similarly for the other off-diagonal terms.

This gives the result that

(A-14) $$\int f_1 f_1 dV = 4$$

Next consider the electron-nucleus interaction terms. Denote

$$H_{en} = - \nabla_i^2 - \frac{2}{r_{ai}} - \frac{2}{r_{bi}}$$

These terms are then

$$I = \sum_{i=1}^{4} \int f_i^* \, H_{en} \, f_i \, dV_i$$

But since the electron number does not affect the result, this is equal to

(A-15) $$I = 4 \int f_1^* \, H_{en1} \, f_1 \, dV_1$$

$$\text{(A-15.1)} \quad I = 4 \int (f_{11}-f_{12}+f_{13}-f_{14}) H_{en1} (f_{11}-f_{12}+f_{13}-f_{14}) dV_1$$

$$\begin{aligned} I = {} & 4 \int f_{11} H_{en1} (f_{11}-f_{12}+f_{13}-f_{14}) dV_1 \\ & - 4 \int f_{12} H_{en1} (f_{11}-f_{12}+f_{13}-f_{14}) dV_1 \\ & + 4 \int f_{13} H_{en1} (f_{11}-f_{12}+f_{13}-f_{14}) dV_1 \\ & - 4 \int f_{14} H_{en1} (f_{11}-f_{12}+f_{13}-f_{14}) dV_1 \end{aligned}$$

In this integral, only one electron is affected by the H_{en1} operator. In the cases of off-diagonal terms, such as

$$\int f_{11} H_{en1} f_{13} dV_1$$

the components in each case break down into integrals of the form

$$\text{(A-16)} \quad \sum_{i=1}^{4} \int \left[\phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\right] H_{en1} \left[\phi_u(1)\phi_g(2)\phi_g(3)\phi_u(4)\right] dV_1$$

$$\begin{aligned} = {} & \int \phi_g(1) H_{en1} \phi_u(1) dV_1 \int \phi_u(2)\phi_g(2) dV_2 \int \phi_u(3)\phi_g(3) dV_3 \int \phi_g(4)\phi_u(4) dV_4 \\ & + \int \phi_g(1)\phi_u(1) dV_1 \int \phi_u(2) H_{en1} \phi_g(2) dV_2 \int \phi_u(3)\phi_g(3) dV_3 \int \phi_g(4)\phi_u(4) dV_4 \\ & + \int \phi_g(1)\phi_u(1) dV_1 \int \phi_u(2)\phi_g(2) dV_2 \int \phi_u(3) H_{en1} \phi_g(3) dV_3 \int \phi_g(4)\phi_u(4) dV_4 \\ & + \int \phi_g(1)\phi_u(1) dV_1 \int \phi_u(2)\phi_g(2) dV_2 \int \phi_u(3)\phi_g(3) dV_3 \int \phi_g(4) H_{en1} \phi_u(4) dV_4 \end{aligned}$$

In each such circumstance, there will always be a pair of component integrals of the form

$$\int \phi_g(1)H_{en1}\phi_u(1)dV_1 \int \phi_u(2)\phi_g(2)dV_2 \cdots$$

One of the two integrals will always be zero. Thus, for the same reasons as in the first case considered, the off-diagonal terms must be zero, and

$$(\text{A-16.2}) \quad I = 4\int f_{11}H_{en1}f_{11}dV_1 + 4\int f_{12}H_{en1}f_{12}dV_1$$

$$+ 4\int f_{13}H_{en1}f_{13}dV_1 + 4\int f_{14}H_{en1}f_{14}dV_1$$

This can be further expanded, noting that the integrals over all electrons except the first are now unity, as

$$I = 4\{\int \phi_g(1)H_{en1}\phi_g(1)dV_1 + \int \phi_g(1)H_{en1}\phi_g(1)dV_1$$

$$+ \int \phi_u(1)H_{en1}\phi_u(1)dV_1 + \int \phi_u(1)H_{en1}\phi_u(1)dV_1\}$$

$$I = 4\{2\int \phi_g(1)H_{en1}\phi_g(1)dV_1 + 2\int \phi_u(1)H_{en1}\phi_u(1)dV_1\}$$

$$(\text{A-17}) \quad I = 4\{2H_g + 2H_u\}$$

Turning finally to the last of the terms in Eq. (A-8),

$$(\text{A-18}) \quad J = \{\int f_1^*(\sum_{i>j=1}^{4} \frac{2}{r_{ij}})f_1 dV\}$$

In this integral, unlike the previous cases, there are terms remaining from many integrals which were previously zero. Equation (A-18) may be expanded as

$$\text{(A-18.1)}\quad J = \int (f_{11}-f_{12}+f_{13}-f_{14}) \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right]$$

$$X \quad (f_{11}-f_{12}+f_{13}-f_{14})dV_1$$

$$J = \int f_{11}\left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{34}} + \frac{2}{r_{24}}\right](f_{11}-f_{12}+f_{13}-f_{14})dV_1$$

$$- \int f_{12} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right](f_{11}-f_{12}+f_{13}-f_{14})dV$$

$$+ \int f_{13} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right](f_{11}-f_{12}+f_{13}-f_{14})dV$$

$$- \int f_{14} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right](f_{11}-f_{12}+f_{13}-f_{14})dV$$

This expands into a total of ninety-six terms which must be regrouped. It is readily apparent that the four diagonal terms are combinable, as are terms of the form $\int f_{11}(\sum_{i>j=1}^{4} \frac{2}{r_{ij}})f_{12}dV$. After one combines terms, Eq. (A-18.1) may be written as

$$\text{(A-19)}\quad J = 4 \int f_{11} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right]f_{11}dV$$

$$+ 2\{(-) \int f_{11} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right]f_{12}dV$$

$$+ \int f_{11} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right]f_{13}dV$$

$$- \int f_{11} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right] f_{14} dV$$

$$- \int f_{12} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right] f_{13} dV$$

$$+ \int f_{12} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right] f_{14} dV$$

$$+ \int f_{13} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right] f_{14} dV\}$$

Proceed by explicitly expanding the diagonal term first:

$$J_{11} = \int \left[\phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\right]\left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right]$$

$$\left[\phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\right] dV$$

$$J_{11} = \iint \phi_g(1)\phi_u(2)\left(\frac{2}{r_{12}}\right)\phi_g(1)\phi_u(2) dV_1 dV_2 \int \phi_u(3)\phi_u(3) dV_3 \int \phi_g(4)\phi_g(4) dV_4$$

$$+ \iint \phi_g(1)\phi_u(3)\left(\frac{2}{r_{13}}\right)\phi_g(1)\phi_u(3) dV_1 dV_3 \int \phi_u(2)\phi_u(2) dV_2 \int \phi_g(4)\phi_g(4) dV_4$$

$$+ \iint \phi_g(1)\phi_g(4)\left(\frac{2}{r_{14}}\right)\phi_g(1)\phi_g(4) dV_1 dV_4 \int \phi_u(2)\phi_u(2) dV_2 \int \phi_u(3)\phi_u(3) dV_3$$

$$+ \iint \phi_u(2)\phi_u(3)\left(\frac{2}{r_{23}}\right) \phi_u(2)\phi_u(3) dV_2 dV_3 \int \phi_g(1)\phi_g(1) dV_1 \int \phi_g(4)\phi_g(4) dV_4$$

$$+ \iint \phi_u(2)\phi_g(4)\left(\frac{2}{r_{24}}\right)\phi_u(2)\phi_g(4) dV_2 dV_4 \int \phi_g(1)\phi_g(1) dV_1 \int \phi_u(3)\phi_u(3) dV_3$$

$$+ \iint \phi_u(3)\phi_g(4)\left(\frac{2}{r_{34}}\right)\phi_u(3)\phi_g(4) dV_3 dV_4 \int \phi_g(1)\phi_g(1) dV_1 \int \phi_u(2)\phi_u(2) dV_2$$

Here, all integrals not involving a $(\frac{2}{r_{ij}})$ factor are unity. The others may then be combined into

$$\text{(A-20)} \quad J_{11} = \{ \iint \phi_g(1)\phi_g(4)(\frac{2}{r_{14}})\phi_g(1)\phi_g(4)dV_1dV_4$$

$$+ \iint \phi_u(2)\phi_u(3)(\frac{2}{r_{23}})\phi_u(2)\phi_u(3)dV_2dV_3$$

$$+ 4 \iint \phi_g(1)\phi_u(2)(\frac{2}{r_{12}})\phi_g(1)\phi_u(2)dV_1dV_2$$

Expanding the next term in Eq. (A-19) gives

$$J_{12} = \int f_{11} \left[\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right] f_{12}dV$$

$$= \int \left[\phi_g(1)\phi_u(2)\phi_u(3)\phi_g(4)\right](\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}})$$

$$\left[\phi_g(1)\phi_u(2)\phi_g(3)\phi_u(4)\right] dV$$

$$J_{12} = \iint \phi_u(3)\phi_g(4)(\frac{2}{r_{34}})\phi_g(3)\phi_u(4)dV_3dV_4$$

where the terms involving factors of the form

$$\text{(A-13.1)} \quad \int \phi_u(3)\phi_g(3)dV_3 = 0$$

have been dropped. Similarly, the third term

$$J_{13} = \int f_{11}\left(\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right) f_{13} dV = 0$$

since there will always be terms of the form of Eq. (A-13.1) remaining.

The fourth term of Eq. (A-19) is

$$J_{14} = \int f_{11}\left(\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right) f_{14} dV$$

$$J_{14} = \iint \phi_g(1)\phi_u(2)\left(\frac{2}{r_{12}}\right)\phi_u(1)\phi_g(2) dV_1 dV_2$$

after cancellation of terms.

The next term in Eq. (A-19) is

$$J_{23} = \int f_{12}\left(\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right) f_{13} dV$$

$$J_{23} = \iint \phi_g(1)\phi_u(2)\left(\frac{2}{r_{12}}\right)\phi_u(1)\phi_g(2) dV_1 dV_2$$

Continuing with the next term of Eq. (A-19),

$$J_{24} = \int f_{12}\left(\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right) f_{14} dV$$

$$J_{24} = 0$$

since each term has a factor of the form of Eq. (A-13.1).

The final term in Eq. (A-19) is

$$J_{34} = \int f_{13}\left(\frac{2}{r_{12}} + \frac{2}{r_{13}} + \frac{2}{r_{14}} + \frac{2}{r_{23}} + \frac{2}{r_{24}} + \frac{2}{r_{34}}\right) f_{14} dV$$

$$J_{34} = \iint \phi_g(3)\phi_u(4)(\frac{2}{r_{34}})\phi_u(3)\phi_g(4)dV_3dV_4$$

Thus, combining all the non zero terms into (A-19) gives

(A-21) $J = 4\ J_{11} - 2\left[J_{12}-J_{13}+J_{14}+J_{23}-J_{24}+J_{34}\right]$

$J = 4\ J_{11} - 2\left[4\ J_{12}\right]$

$J = 4\left[J_{11} - 2\ J_{12}\right]$

The term J_{11} is given, in the notation of the main text, as

(A-20.1) $J_{11} = J_{gg} + J_{uu} + 4\ J_{gu}$

and

(A-22) $J_{12} = 2\ K_{gu}$

The combination of each of these terms into the energy, given as Eq. (A-8), gives Eq. (9) in the main body of the text.

APPENDIX B

EVALUATION OF INTEGRALS ENCOUNTERED IN THE GROUND STATE ENERGY CALCULATION

Much of the material here is also presented in Slater (51), his Appendix Six in particular containing much background information on these calculations. One term, J_{gg3}, will be presented in detail as representative of the method of solution, and to present the method of evaluation of one type of problem integral.

CONSTANTS AND PRIMARY INTEGRALS

The wavefunctions Φ_g and Φ_u are normalized wavefunctions, that is

$$\int \Phi_g^* \Phi_g \, dV = 1 \qquad \text{and} \qquad \int \Phi_u^* \Phi_u \, dV = 1 \ .$$

The N_g and N_u are the normalization constants. They are given by

$$\int \Phi_g^* \Phi_g dV = \int N_g(\chi_a+\chi_b) N_g(\chi_a+\chi_b) \, dV$$

or

$$N_g^2 \int (\chi_a+\chi_b)(\chi_a+\chi_b) \, dV = 1 \ .$$

Thus

$$N_g^2 \left\{ \int \chi_a\chi_a \, dV + 2\int \chi_a\chi_b \, dV + \int \chi_b\chi_b \, dV \right\} = 1 \quad .$$

But the atomic wavefunctions are already normalized, so that

$$\int \chi_a\chi_a \, dV = \int \chi_b\chi_b \, dV = 1 \ .$$

This gives the relation that

$$N_g^2 \ \{ 1 + 2 \int \chi_a \chi_b \, dV + 1 \} = 1.$$

So

$$N_g^2 \ \{ 1 + \int \chi_a \chi_b \, dV \} = 1/2 \quad .$$

Denoting $\int \chi_a \chi_b \, dV = S$, then

$$N_g^2 = (\frac{1}{1+S})(1/2) \ , \text{ or}$$

(B-1) $$N_g = \frac{1}{\sqrt{2}} \ (\frac{1}{1+S})^{\frac{1}{2}} \ .$$

Similarly,

$$N_u^2 \ \{ 1 + \int \chi_a' \chi_b' \, dV \} = 1/2 \ .$$

These atomic wavefunctions are also normalized. Then

(B-2) $$N_u = \frac{1}{\sqrt{2} \ (1+T)^{\frac{1}{2}}}$$

where

$$T = \int \chi_a' \chi_b' \, dV \ .$$

It still remains to determine S and T.

$$S = \int \chi_a \chi_b \, dV = \frac{\alpha^3}{\pi} \int e^{-\alpha r_a} e^{-\alpha r_b} \, dV$$

(B-3) $$S = \frac{\alpha^3}{\pi} \int_{-1}^{1} \int_{1}^{\infty} (\lambda^2 - \mu^2) \ e^{-\alpha R \lambda} \ d\lambda \ d\mu \ (\frac{\pi R^3}{4}) \quad ,$$

where a conversion to confocal coordinates has been made to facilitate the evaluation of this integral. Here, it is easily seen that

$$S = \frac{\alpha^3 R^3}{4} \ \{ \int_{-1}^{1} d\mu \int_{1}^{\infty} e^{-\alpha R \lambda} d\lambda - \int_{-1}^{1} d\mu \int_{1}^{\infty} e^{-\alpha R \lambda} d\lambda$$

TABLE B-I

FREQUENTLY ENCOUNTERED CONFOCAL INTEGRALS

$$\int_1^\infty \lambda \quad e^{-\alpha R\lambda} \, d\lambda = \frac{(n!)e^{-\alpha R}}{(\alpha R)^{n+1}} \left(1 + \alpha R + \frac{(\alpha R)^2}{2!} + \ . \ . \ . + \frac{\alpha^n R^n}{n!} \right)$$

$$\int_1^{\lambda_2} e^{-k\lambda_1} \left(\lambda_1 - \frac{1}{3}\right) d\lambda = \frac{2e^{-k\lambda_2}}{k^2} \left(1 + k\lambda_2 + \frac{k}{2}\left(\lambda_2 - \frac{1}{3} \right) \right)$$

$$\int_{-1}^{1}\int_1^\infty (\lambda+\mu) \, e^{-\alpha R\lambda} \, d\lambda \, d\mu = \frac{2e^{-\alpha R} (1 + \alpha R)}{\alpha^2 R^2}$$

$$\int_{-1}^{1} d\mu = 2$$

$$\int_{-1}^{1} \mu^2 \, d\mu = \frac{2}{3}$$

$$\int_{-1}^{1} \mu^4 \, d\mu = \frac{2}{5}$$

$$\int_{-1}^{1} \mu^{2n} \, d\mu = \frac{2}{2n+1}$$

$$\int_{-1}^{1} \mu^{2n+1} \, d\mu = 0 \text{ , n integer}$$

$$\int_{-1}^{1} e^{-\alpha R\mu} \, d\mu = \frac{e^{\alpha R} - e^{-\alpha R}}{\alpha R}$$

$$\int_{-1}^{1} \mu e^{-\alpha R\mu} \, d\mu = \frac{e^{\alpha R} (\alpha R + 1) + e^{-\alpha R} (\alpha R + 1)}{\alpha^2 R^2}$$

$$\int_{-1}^{1} \mu^2 \, e^{-\alpha R\mu} \, d\mu = \left(\frac{1}{\alpha^3 R^3}\right) \{ e^{\alpha R}(2 - 2\alpha R + \alpha^2 R^2) + e^{-\alpha R}(2 + 2\alpha R + \alpha^2 R^2)\}$$

Each of these integrals is easily evaluated; the final value for S is

$$S = e^{-\alpha R} \{ 1 + \alpha R + \frac{\alpha^2 R^2}{3} \} \ .$$

Or, letting $w = \alpha R$,

$$S = (1 + w + \frac{w^2}{3}) e^{-w} \ . \tag{B-4}$$

In an identical manner,

$$T = \int \chi_a' \chi_b' \, dV = \frac{\gamma^3}{\pi} \int e^{-\gamma r_a} e^{-\gamma r_b} \, dV \tag{B-5}$$

It is immediately seen by comparison with Eq. (B-3) that the two integrals are identical except for the interchange of one constant for another (i.e., γ for α). The result for Eq. (B-5) is thus given by

$$T = (1 + \gamma R + \frac{\gamma^2 R^2}{3}) e^{-\gamma R} \ .$$

Letting $x = \gamma R$, this may be rewritten

$$T = (1 + x + \frac{x^2}{3}) e^{-x} \ . \tag{B-6}$$

EVALUATION OF J_{gg3} INTEGRAL

The J_{gg3} integral will be worked out in detail, to illustrate the technique involved in the solution of the terms given in Chapter IV, and to demonstrate the method of evaluation of the ill-behaved integrals encountered in this and other terms.

The problem that arises with the J_{gg3} and similar integrals is that the integration must be carried out in confocal coordinates, where the interelectronic separation $(\frac{1}{r_{12}})$ is a complicated expression. Its value is given as Eq. (23) in Chapter IV.

The terms it will be necessary to deal with using this expansion are of the form

$$\int f(1) \left[\int f(2)\left(\frac{1}{r_{12}}\right) dV_2 \right] dV_1 \quad ,$$

so one must first evaluate the integral

$$\text{(B-7)} \qquad I_{gg} = \int f(2)\left(\frac{1}{r_{12}}\right) dV_2 \quad .$$

Only the case of

$$f(2) = \chi_a(2)\chi_b(2) = \frac{\alpha^3}{\pi} e^{-\alpha(r_{a_2}+r_{b_2})}$$

need be considered, as

$$f(2) = \chi_a'(2)\chi_b'(2) = \frac{\gamma^3}{\pi} e^{-\gamma(r_{a_2}+r_{b_2})}$$

is adequately treated by the interchange of γ for α. Using the expansion of Eq. (23), Eq. (B-7) becomes

$$\text{(B-7.1)} \qquad I_{gg} = \frac{\alpha^3}{\pi} \int_0^{2\pi} \int_1^1 \int_1^\infty \{(\lambda_2^2 - \mu_2^2)\left(\frac{2}{R}\right) \sum_{k=0}^{\infty} \sum_{m=-k}^{k} (-1)^m (2k+1)$$

$$\left[\frac{(k-|m|)!}{(k+|m|)!} \right]^2 P_k^{|m|}\left[\lambda(a)\right] Q_k^{|m|}\left[\lambda(b)\right] P_k^{|m|}(\mu_1) P_k^{|m|}(\mu_2) e^{-im(\phi_2-\phi_1)} e^{-\alpha R\lambda_2}$$

$$d\lambda_2 d\mu_2 d\phi_2 \}$$

The integration over ϕ_2 will yield zero except when $m=0$, since

$$\int_0^{2\pi} e^{-ikx} dx = \left(\frac{1}{ik}\right)(e^0 - e^{-2i\pi}) \quad .$$

Physically, the vanishing of Eq. (B-7.1) except for $m=0$ arises from the fact that an S-type wavefunction has no dependence on azimuthal angle. Thereby, Eq. (B-7.1) simplifies to

(B-7.2) $$I_{gg} = \alpha^3 R^2 \sum_{k=0}^{\infty} (2k+1) \int_{-1}^{1} \int_{1}^{\infty} (\lambda_2^2 - \mu_2^2)\, e^{-\alpha R \lambda_2} P_k[\lambda(a)]\, Q_k[\lambda(b)]\, P_k(\mu_1)\, P_k(\mu_2)\, d\lambda_2 d\mu_2$$

Now the factors involved in the μ_2 integration are expressable in terms of Legendre polynomials by use of tabulated values:

$$(\lambda_2^2 - \mu_2^2) = (\lambda_2^2 - \frac{1}{3})\, P_0(\mu_2) - \frac{2}{3} P_2(\mu_2)$$

Making use of the orthogonality properties of the Legendre polynomials, I_{gg} becomes

(B-7.3) $$I_{gg} = \alpha^3 R^2 \{ \int_1^{\infty} (\lambda_2^2 - \frac{1}{3}) e^{-\alpha R \lambda_2} P_0[\lambda(a)]\, Q_0[\lambda(b)]\, P_0(\mu_1)\, d\lambda_2 - \frac{4}{3} \int_1^{\infty} P_2[\lambda(a)]\, Q_2[\lambda(b)]\, P_2(\mu_1) e^{-\alpha R \lambda_2}\, d\lambda_2 \}$$

Substitution of tabulated values fo P_0, P_2, Q_0, and Q_2, and reexpression of the integral in terms of the actual functions λ_1 and λ_2 in place of the dummy functions $\lambda(a)$ and $\lambda(b)$ yields

(B-7.4) $$\begin{aligned} I_{gg} = \alpha^3 R^2 \{ & \ell n(\frac{\lambda_1+1}{\lambda_1-1}) \int_1^{\lambda_1} (\lambda_2^2 - \frac{1}{3}) e^{-\alpha R \lambda_2} d\lambda_2 \\ & + \int_{\lambda_1}^{\infty} (\lambda_2^2 - \frac{1}{3})\, \ell n(\frac{\lambda_2+1}{\lambda_2-1})\, e^{-\alpha R \lambda_2} d\lambda_2 \\ & - \frac{9}{4} (\mu^2 - \frac{1}{3}) \{ (\lambda_1^2 - \frac{1}{3})\, \ell n(\frac{\lambda_1+1}{\lambda_1-1}) - 2\lambda_1 \} \int_1^{\lambda_1} e^{-\alpha R \lambda_2} (\lambda_2^2 - \frac{1}{3})\, d\lambda_2 \\ & - \frac{9}{4} (\mu^2 - \frac{1}{3}) (\lambda_1^2 - \frac{1}{3}) \int_{\lambda_1}^{\infty} [(\lambda_2^2 - \frac{1}{3})\, \ell n(\frac{\lambda_2+1}{\lambda_2-1}) - 2\lambda_2]\, e^{-\alpha R \lambda_2}\, d\lambda_2 \} \end{aligned}$$

where the subscript on μ has been supressed as superfluous.

The process of solution which will be followed is one of breaking these integrals up for separate handling. The first of these is

$$\text{(B-8)} \qquad I_1 = \int_1^{\lambda_1} (\lambda_2^2 - \frac{1}{3}) \, e^{-\alpha R \lambda_2} \, d\lambda_2 \; .$$

This integral may be evaluated easily as

$$\text{(B-8.1)} \qquad I_1 = (\frac{2}{\alpha^3 R^3}) \{ e^{-\alpha R} (1 + \alpha R + \frac{\alpha^2 R^2}{2}) - e^{-\alpha R \lambda} (1 + \alpha R \lambda + \frac{\alpha^2 R^2}{2} (\lambda^2 - \frac{1}{3})) \}$$

Continuing,

$$\text{(B-9)} \qquad I_2 = \int_{\lambda_1}^{\infty} (\lambda_2^2 - \frac{1}{3}) \, e^{-\alpha R \lambda_2} \, \ell n (\frac{\lambda_2 + 1}{\lambda_2 - 1}) \, d\lambda_2$$

From the symmetry of the logarithmic term, it is obvious that there are two integrals of identical form to be considered, each depending only on the sign of the constant in the argument. It is therefore possible to replace the constants +1 and -1 in this term by the single constant -a, and by later setting a=+1 or a=-1 obtain the specific form desired. Integration by parts, followed by a change of variables in Eq. (B-9) gives

$$\text{(B-9.1)} \qquad I_2 = \frac{2}{\alpha^3 R^3} \{ \ell n(\lambda_1 - a) e^{-\alpha R \lambda_1} [1 + \alpha R \lambda_1 + \frac{\alpha^2 R^2}{2} (\lambda_1^2 - \frac{1}{3})] + e^{-a\alpha R} (1 - a\alpha R + \frac{1}{3}) \, Ei(-\alpha R(\lambda_1 - a)) + \frac{\alpha R - a\alpha^2 R^2}{\alpha R} \, e^{-\alpha R(\lambda_1 - a)} + \frac{\alpha^2 R^2}{2\alpha^2 R^2} \, e^{-\alpha R(\lambda_1 - a)} (1 + \alpha R \lambda_1 + a\alpha R) \}$$

Evaluating Eq. (B-9.1) for the two values of a allows the result to be obtained for I_2 that

$$I_2 = \frac{2e^{-\alpha R\lambda}}{\alpha^3R^3}\{1 + \alpha R\lambda + \frac{\alpha^2R^2}{2}(\lambda^2 - \frac{1}{3})\}\{\ln(\lambda+1) - \ln(\lambda-1)\}$$ (B-9.2)

$$+ \frac{2e^{-\alpha R}}{\alpha^3R^3}(1 + \alpha R + \frac{\alpha^2R^2}{3})\ Ei(-\alpha R(\lambda-1)) - \frac{2e^{+\alpha R}}{\alpha^3R^3}(1 - \alpha R$$

$$+ \frac{\alpha^2R^2}{3})\ Ei(-\alpha R(\lambda+1)) - \frac{2e^{-\alpha R\lambda}}{\alpha^2R^2}$$

Substitution of the values of the integrals I_1 and I_2 into Eq. (B-7.4) for I_{gg} is now possible. Note that the coefficient of the $Ei(-\alpha R(\lambda-1))$ term is just the overlap integral S.

Define a new function

$$S' = e^{+\alpha R}(1 - \alpha R + \frac{\alpha^2R^2}{3})$$

as the coefficient of the $Ei(-\alpha R(\lambda+1))$ term. Substitution of values for I_1 and I_2 then gives

$$I_{gg} = \frac{2}{R}\{1 - \frac{9}{4}(\mu^2 - \frac{1}{3})\}\{S \ln(\frac{\lambda+1}{\lambda-1}) - S'\ Ei(-\alpha R(\lambda+1))$$ (B-7.5)

$$+ S\ Ei(-\alpha R(\lambda-1)) - \alpha R e^{-\alpha R\lambda}\} + \frac{9}{R}(\mu^2 - \frac{1}{3})\{\lambda S - e^{-\alpha R\lambda}(\frac{\alpha R}{6} + \lambda + \frac{\alpha R\lambda^2}{2}) .$$

Equation (B-7.5) is the initial integral for a good many of the integrals involved in the ground state energy calculation.

Next, consider

$$J_{gg3} = \int \chi_a(1)\chi_b(1) I_{gg}\ dV_1$$ (B-10)

$$J_{gg3} = \frac{\alpha^3}{\pi}\int e^{-\alpha(r\quad +r\quad)} I_{gg}\ dV_1$$

Transformation to confocal coordinates gives the form

$$J_{gg3} = \frac{\alpha^3R^3}{4}\int_{-1}^{1}\int_{1}^{\infty}\{(\lambda^2 - \frac{1}{3}) - (\mu^2 - \frac{1}{3})\}\ e^{-\alpha R\lambda} I_{gg}\ d\lambda\ d\mu$$ (B-10.1)

where $\frac{1}{3}$ has been added and subtracted in the $(\lambda^2 - \mu^2)$ term in order to obtain the factor $(\mu^2 - \frac{1}{3})$, which is directly proportional to $P_2(\mu)$. This allows the orthogonality properties of the Legendre polynomials to be fully exploited in simplifying the result. Using the relation that

$$\mu^2 - \frac{1}{3} = \frac{3}{2} P_2(\mu)$$

a nonzero contribution to the integral over μ arises only from the products between terms not involving μ with like terms and from products between terms proportional to μ^2. Then, noting

$$\int_1^1 (\mu^2 - \frac{1}{3})^2 d\mu = \frac{8}{45}$$

$$\text{(B-10.2)} \qquad J_{gg3} = \frac{6\alpha^3 R^3}{5} \int_1^\infty (\lambda^2 - \frac{1}{3})\, e^{-\alpha R\lambda}\, \mathscr{s}(\lambda)\, d\lambda$$
$$- \frac{2\alpha^3 R^3}{5} \int_1^\infty \{ e^{-\alpha R\lambda} \lambda\, S - e^{-2\alpha R\lambda} (\frac{\alpha R}{6} - \lambda - \frac{\alpha R\lambda^2}{2}) \; d\lambda$$

where

$$\mathscr{s}(\lambda) = S\, \ell n(\frac{\lambda+1}{\lambda-1}) - S'\, Ei(-\alpha R(\lambda+1)) + S\, Ei(-\alpha R(\lambda-1)) - \alpha R e^{-\alpha R\lambda} .$$

It is desirable to investigate the improper integrals first. Consider the integrals over the $Ei(x-1)$ functions. It is necessary to proceed by an integration by parts, with the lower limit replaced by δ, since each integral is improper at the lower limit. Again let $-a$ be used in place of the $+1$ and the -1, and investigate the integral

$$\text{(B-11)} \qquad \int_\delta^\infty e^{-\alpha R\lambda} (\lambda^2 - \frac{1}{3})\, Ei(-\alpha R(\lambda - a))\, d\lambda .$$

Integration by parts gives

$$\text{(B-11.1)} \qquad \frac{2}{\alpha^3R^3}\, Ei\,(-\alpha R(\delta-a))e^{-\alpha R\delta}\{1+\alpha\delta R \;+ \frac{\alpha^2R^2}{2}(\delta^2-\frac{1}{3})\}$$

$$- \frac{2}{\alpha^3R^3}\, Ei(-2\alpha R(\delta-a))\{1 + a\alpha R + \frac{\alpha^2R^2}{2}\}\; e^{-a}$$

$$+ \frac{1}{\alpha^4R^4}\, e^{-a\alpha R}(\;\alpha R + a\alpha^2R^2)\; e^{-2\alpha R(\delta-a)}$$

$$+ \frac{1}{4\alpha^3R^3}e^{-a\alpha R}\; e^{-2\alpha R(\delta-a)}\; (1 + 2\alpha R -2a\alpha R) \quad .$$

Combination of Eq. (B-11.1) with the integral over $\ell n(\frac{\lambda+1}{\lambda-1})$ of Eq. (B-10.2) (noting the difficulty with the lower limit in both cases), and taking the $\lim\limits_{\delta\to 1}$ where this limit is well-defined, gives

$$\text{(B-10.3)} \qquad J_{gg3} = \frac{12}{5R}\,\{S\big[S\;\ell n(2)\; -S\;\ell n(\delta-1)\; -S'\; Ei(-2\alpha R)\; -\alpha Re^{-\alpha R}$$

$$+S\; Ei(-\alpha R(\delta-1))\big] - S'\big[S\; Ei(-2\alpha R)\; -S'\; Ei(-4\alpha R) + \frac{5}{8}\, e^{-3\alpha R}\big]$$

$$+S\big[S\; Ei(-\alpha R(\delta-1))\; -S\; Ei(-2\alpha R(\delta-1))\; +(\frac{5}{8} + \frac{\alpha R}{2})e^{-\alpha R}\;\big]\;\}$$

$$- \frac{6\alpha^4R^3}{5}\int_1^{\infty} e^{-2\alpha R\lambda}(\lambda^2-\frac{1}{3})\; d\lambda - \frac{2S\alpha^3R^2}{5}\int_1^{\infty} e^{-\alpha R\lambda}\; d\lambda$$

$$+ \frac{2\alpha^3R^2}{5}\int_1^{\infty}(\;\frac{\alpha R}{6} + \lambda + \frac{\alpha R\lambda^2}{2}\;)\; e^{-2\alpha R\lambda}\; d\lambda \quad .$$

Since the terms for which $\lim\limits_{\delta\to 1}$ are not well-defined all have the same coefficient, S^2 , they may be grouped together, as

$$\text{(B-12)} \qquad \Delta \;=\; \{-\;\ell n(\delta-1)\; +2\; Ei(-\alpha R(\delta-1))\; -\; Ei(-2\alpha R(\delta-1))\}$$

By expressing the Ei function in terms of the integral which serves to define it, and rearranging, it may be demonstrated that this term behaves in an acceptable fashion in the limit $\delta\to 1$.

$$\text{(B-12.1)} \qquad \Delta = \lim_{\delta\to}\;\{\;-\;\ell n(\delta-1)\; -2\int_{\alpha R(\delta-1)}^{\infty} \frac{e^{-x}\,dx}{x} + \int_{2\alpha R(\delta-1)}^{\infty} \frac{e^{-x}\,dx}{x}\;\}$$

Transform the integrals in Eq. (B-12.1) by adding and subtracting the same quantity to the equation:

$$\text{(B-12.2)}\quad \Delta = \lim_{\delta\to 1}\{-\ln(\delta-1) -2\int_{\alpha R(\delta-1)}^{\infty}\frac{e^{-x}\,dx}{x} -2\int_{\alpha R(\delta-1)}^{1}\frac{dx}{x} +2\int_{\alpha R(\delta-1)}^{1}\frac{dx}{x} +\int_{2\alpha R(\delta-1)}^{\infty}\frac{e^{-x}\,dx}{x} +\int_{2\alpha R(\delta-1)}^{1}\frac{dx}{x} -\int_{2\alpha R(\delta-1)}^{1}\frac{dx}{x}\}$$

Next, combine the terms into single integrals, giving

$$\text{(B-12.3)}\quad \Delta = \lim_{\delta\to 1}\{-\ln(\delta-1) +2\int_{\alpha R(\delta-1)}\frac{(1-e^{-x})}{x}\,dx -2\int_{1}^{\infty}\frac{e^{-x}\,dx}{x} -\int_{2\alpha R(\delta-1)}^{1}\frac{(1-e^{-x})}{x}\,dx +\int_{1}^{\infty}\frac{e^{-x}\,dx}{x} +2\ln(\alpha R) +2\ln(\delta-1) -\ln(2) -\ln(\alpha R) -\ln(\delta-1)$$

Since the terms $\ln(\delta-1)$ add out, then

$$\text{(B-12.4)}\quad \Delta = \int_{0}^{1}\frac{(1-e^{-x})}{x}\,dx - \int_{1}^{\infty}\frac{e^{-x}\,dx}{x} + \ln(\alpha R) - \ln(2)$$

The first two integrals serve as a definition of Euler's constant, C.

Thus $\quad \Delta = C + \ln(w) - \ln(2)$.

The terms not yet evaluated are elementary; the final result for J_{gg3} is

$$\text{(B-10.4)}\quad J_{gg3} = \frac{12}{5R}\{S^2(C+\ln(w)) + (S')^2\,Ei(-4\alpha R) - 2SS'\,Ei(-2\alpha R)\} + e^{-2w}\left(\frac{5}{4} - \frac{23w}{10} - \frac{6w^2}{5} - \frac{2w^3}{15}\right) .$$

APPENDIX C

COMPARISON OF RESULTS OBTAINED WITH THOSE OF HUZINAGA FOR He-He

In the paper of Huzinaga (51), detailed values are given for the individual integrals only for the case of R = 1 Bohr, and are given for three sets of alpha and gamma values. These have been tested explicitly for agreement, as have other values given by Huzinaga in the form of the energy of the state for a given R.value. The following table presents the comparison of the results obtained by both methods, for the value R = 1 Bohr. The results of Huzinaga have been converted to Rydbergs from Hartrees (each equal to two Rydbergs).

TERM	HUZINAGA	THIS CALCULATION
	Alpha = Gamma = 1.75	
H_{gg}	-8.080478	-8.08132 (alpha=1.7505)
H_{uu}	-5.3238	-5.3238
J_{gg}	1.800708	1.90114
J_{uu}	1.970024	1.970024
J_{gu}	1.871924	1.872140
K_{gu}	-0.513378	-0.513482
E_{total}	-8.476912	-8.47750
	Alpha = 2.25; Gamma = 1.25	
H_{gg}	-8.63269	-8.632688
H_{uu}	-4.97937	-4.97937
J_{gg}	2.29911	2.299109
J_{uu}	1.49188	1.491879
J_{gu}	1.72451	1.724513
K_{gu}	0.438298	0.38693
E_{total}	-9.41168	-9.37126

TERM	HUZINAGA	THIS CALCULATION
Alpha = 2.5; Gamma = 1.0		
H_{gg}	-8.69146	-8.6914597
H_{uu}	-4.55023	-4.550229
J_{gg}	2.47925	2.479253
J_{uu}	1.22889	1.228894
J_{gu}	1.53580	1.535799
K_{gu}	0.33758	0.21041
E_{total}	-9.29956	-9.18196

All values given are for an internuclear separation R of R=1.00 Bohr.

APPENDIX D

CHARACTERISTICS AND PRODUCTION OF V_k, H, AND F COLOUR CENTERS

There exists extensive literature dealing with colour centers, principally the F center (39-41), but also dealing with the V_k and H centers (38, 59-65). These are not the only types of colour centers observed experimentally, even in alkali halides, but these are the centers of immediate interest in relation to the breakdown problem. These centers are the prototype colour centers; many of the other identified types are related directly to these centers, and are clusters of two or more simple centers. Ivey (66) has written a monograph on electroluminescence and related effects which is also of interest in this connection. In this section, the interest will be focussed principally on the characteristics of the V_k, H, and F centers and their production mechanisms which are most directly related to the breakdown problem. For a more complete treatment, the work of Townsend and Kelly (41) and that of Schulman and Compton (40) make excellent starting points for the recent literature, while the paper of Dienes (38) is an excellent short discussion of the production mechanism of both V_k and the paired H and F centers. The discussion which follows will follow, in large measure, the works of both Dienes (38) and that of Townsend and Kelly (41). Additional information concerning the dynamics of the interactions of these centers with the host lattice is given by Stoneham (68).

The F center consists of a negative ion vacancy, in which an electron is trapped to neutralize the charge of the region. The center is normally produced as an F (also known as an α center), and then traps an electron. It is optically the least energetic of the centers mentioned, and has the longest lifetime at room temperatures. The F center is the dominant colour center in the alkali halides. At temperatures above about 150 K, it is possible in some materials for an additional electron to be trapped at the F center, giving rise to an excess local negative charge within the region of the center.

The V_k center is of much more interest in the discussion of breakdown. This center consists of a hole trapped by a pair of negative ions. After trapping the hole, the combination of atoms relaxes toward a common center, in effect forming a molecular ion; this molecular ion is perturbed by the presence of the lattice. In the conditions encountered before breakdown, the V_k center can be formed directly in the perfect lattice by impact ionization. To quote Dienes (38):

> Ionizing radiation knocks off an electron from a Cl^- ion in (KCl) with the electron pushed off into the conduction band. The original Cl^- becomes a neutral chlorine atom (Cl^o). This configuration is unstable, however, with respect to a Cl_2^- molecule. This, the Cl^o grabs part of the electron of the nearest Cl^- and forms a Cl_2^- molecule [as illustrated in Fig. 5]. Thus, the V_k center is a Cl_2^- ion sharing two normal lattice sites.

As shown in Fig. 5, the molecular ion will orient itself along [110] directions in the normal lattice. Under the influence of a strong electric field, however, this orientation will be perturbed by the electric field.

The H center is the complement of the F center; it consists of a Cl_2^- molecular ion occupying a single Cl^- site. This center, illustrated in Fig. 21, is oriented similarly to the V_k center, along the [110] direction. Quantum mechanical calculations by Dienes (57) give the right configuration of the center but the wrong orientation. The orientation of the H center is apparently stabilized by interaction between the center and the halide ions lying at either end of the H-center's axis. Dienes (38) indicates that the H center can move easily along the [110] direction with an activation energy in the range of 0.1-0.2 eV. This motion may be significant in the breakdown process. The analagous motion of the V_k center does not seem to have been studied, but it might be expected to be similar to that of the H center, but probably having a somewhat higher energy of activation, as the interaction of the H center with neighboring ions would tend to reduce that activation energy for motion in an axial direction.

A formation mechanism for the paired F and H centers has been suggested by Pooley (43) whereby the energy available from electron-V_k recombination is used to produce the pair of centers. Dienes (38) describes the process as follows.

The energy available for the formation of the pair of centers due to the recombination of the V_k with an electron is about 9 eV (for KCl). This energy is the sum of the direct electron-hole recombination energy of about 6.4 eV and the potential energy of the two ions once the recombination has taken place (2.6 eV). If the energy is distributed

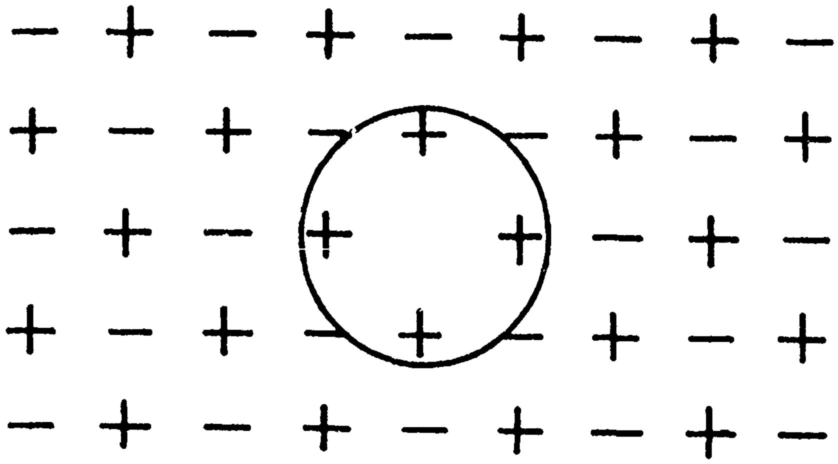


Fig. 20. The F center in an alkali halide crystal. This center consists of a halide vacancy, occupied by a free electron.

(After Townsend and Kelly)

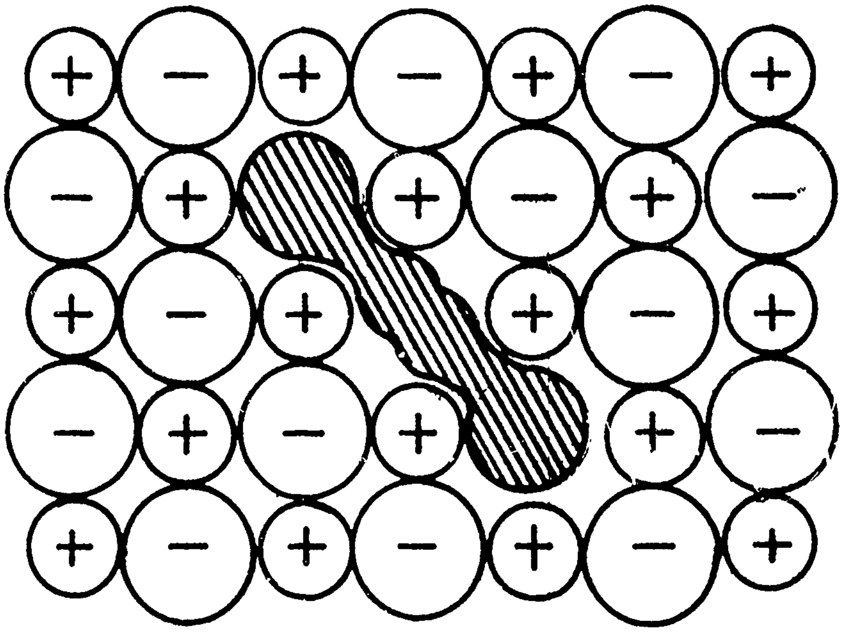


Fig. 21. The H center in an alkali halide crystal. Note that four halide atoms are occupying the lattice spaces normally occupied by three halide ions. (After Townsend and Kelly)

asymmetrically between the two atoms, it is possible to initiate a replacement chain of collisions, moving the Cl^- with the greater kinetic energy into the next cell, thus forming a closely linked F and H pair. As indicated earlier, the energy of activation for motion of the H center once created is small, so the motion will continue along several cells, leading to a displacement of the H center by several unit cells from the F center. It is necessary that the F center retain the excess electron, as the energy of formation of the pair of H and F^+ centers requires additional energy. The replacement sequence will occur along a [110] direction within the crystal. It appears likely that the mechanism leading to the formation of the H and F centers will dominate other defect production mechanisms for higher temperatures (above]50 °K).

The effect upon the H center of the application of an electric field of the magnitudes involved in breakdown should be similar to that described above for the V_k center, but H center mobility is probably higher than that of the V_k center. Motion of an H center entails only a slight displacement of the added Cl^o atom to an adjoining Cl^- site. Thus mobility along crystallographic directions close-packed with Cl^- ions is favored over other directions in highly perfect crystals. In crystals with high elastic stress or high dislocation densities, other paths might be preferred. This provides perspective on the directional effects seen by Davisson, Cooper, and others (mentioned earlier) in breakdown studies.

There exists one other polarization effect which calls for mention in connection with these centers. Both the V_k and the H centers