JILA REPORT #79

PROCEEDINGS

OF

WORKSHOP CONFERENCE ON THE LOWERING OF THE IONIZATION

POTENTIAL AND RELATED PROBLEMS OF THE EQUILIBRIUM PLASMA

edited by

J. Cooper

held at the University of Colorado

on November 12-13, 1965

IMPORTANT NOTICE

This report from the JILA contains unpublished material of a preliminary nature, or of transitory interest, and may not have been subjected to critical technical review. Such reports are issued sporadically as preprints, contract reports or unpublished communications. As such their reproduction, quotation, or citation in the open literature is not permitted without express permission of the author or the Chairman of the JILA. If this material is identified as accepted for publication in the open literature all citations should be made to that journal. If this constitutes a technical report to a sponsoring agency that agency may reproduce this material for further distribution within the government and to agency contractors.

University of Colorado
Boulder, Colorado
July 15, 1966
This research was supported in part by the Advanced Research Projects Agency (Project DEFENDER), monitored by the U. S. Army Research Office-Durham, under Contract DA-31-124-ARO-D-139.
PREFACE

This workshop evolved from a number of discussions at the Joint Institute for Laboratory Astrophysics concerning statistical mechanics of plasma in equilibrium - both from the experimental and theoretical points of view. There were many recent theoretical advances in the treatment of such problems as the plasma partition function and the lowering of the ionization potential, although there were strong disagreements between different workers in this field. In addition, it appeared that many of the experiments which had been done were interpreted in a theoretical framework which was not on firm ground and hence, were difficult to interpret in terms of the correct theoretical questions.

It was the object of this workshop to bring together active theorists and experimenters in this field to acquaint them all with the current thought and, if possible, to resolve some of the differences and to come to some definite conclusions. Since spontaneous communication was an essential feature of this workshop, none of the discussion has been formally recorded in these proceedings. The proceedings were taped and the "Summary of Discussions" and "Editor's Comments" represent the impressions of the Editor, gained in listening to these recordings. Therefore they do not necessarily reflect the feeling of the meeting. At the same time it should be stressed that these proceedings should be considered as unpublished material, and published reference to statements made by a participant should only be made after consultation with him.
Thanks are particularly due to Professor Günter Ecker for acting as Workshop Chairman, and also for preparing the Introduction. The Table of Contents reflects the chronological order of the meeting. Included in the Appendix is a Bibliography on Research on Lowering of the Ionization Potential, kindly supplied by Drs. S. G. Brush and B. H. Armstrong which should be very useful for reference purposes.

Thanks are due to Mrs. R. J. Low, J. Scott Hildum, and R. Alvis and his staff for the organizational aspects and efficient coordination of this conference.

This workshop was sponsored by the Joint Institute for Laboratory Astrophysics using funds made available through an Advanced Research Projects Agency contract. In particular, the assistance of Mrs. M. Brantley at the U. S. Army Research Office is gratefully acknowledged for organizing the travel arrangements for the overseas participants.

May 1966

J. Cooper

Editor and Conference Secretary
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION (by G. Ecker)</td>
<td>1</td>
</tr>
<tr>
<td><strong>Friday, November 12, 1965</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Chairman:</strong> L. M. Branscomb</td>
<td></td>
</tr>
<tr>
<td>I. PROBLEMS OF THE PLASMA IN EQUILIBRIUM</td>
<td>7</td>
</tr>
<tr>
<td>G. Ecker and W. Kröll</td>
<td></td>
</tr>
<tr>
<td>II. STATISTICAL MECHANICS OF PARTIALLY IONIZED PLASMAS</td>
<td>49</td>
</tr>
<tr>
<td>J. L. Jackson and L. S. Klein</td>
<td></td>
</tr>
<tr>
<td>III. EFFECTIVE DISSOCIATION AND IONIZATION ENERGIES IN PARTLY IONIZED</td>
<td>55</td>
</tr>
<tr>
<td>AND DISSOCIATED GASES</td>
<td></td>
</tr>
<tr>
<td>and ON THE EXISTENCE OF NON-PHYSICAL SOLUTIONS TO A SAHA-TYPE EQUATION</td>
<td>79</td>
</tr>
<tr>
<td>IN THE PRESENCE OF LONG-RANGE INTERACTIONS</td>
<td></td>
</tr>
<tr>
<td>A. R. Hochstim</td>
<td></td>
</tr>
<tr>
<td><strong>Chairman:</strong> G. Ecker</td>
<td></td>
</tr>
<tr>
<td>IV. REVIEW OF CURRENT KNOWLEDGE OF EQUILIBRIUM PLASMA STATISTICAL</td>
<td>87</td>
</tr>
<tr>
<td>MECHANICS</td>
<td></td>
</tr>
<tr>
<td>H. DeWitt</td>
<td></td>
</tr>
<tr>
<td>V. THOMAS-FERMI METHODS IN THE DESCRIPTION OF THE PLASMA IN EQUILIBRIUM</td>
<td>109</td>
</tr>
<tr>
<td>J. C. Stewart and K. D. Pyatt, Jr.</td>
<td></td>
</tr>
<tr>
<td>VI. JUSTIFICATIONS OF THE STEWART-PYATT MODEL</td>
<td>131</td>
</tr>
<tr>
<td>B. H. Armstrong</td>
<td></td>
</tr>
<tr>
<td>VII. VERY DENSE PLASMAS IN THE THOMAS-FERMI STATISTICAL MODEL</td>
<td>137</td>
</tr>
<tr>
<td>G. Lehner</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER

Saturday, November 13, 1965

Chairman: J. Cooper

I. THERMAL IONIZATION EQUILIBRIUM IN HYDROGEN PLASMAS . . . . . . . . . 151
   H. R. Griem

II. THE PLASMA IN EQUILIBRIUM: EXPERIMENTAL ASPECTS . . . . . . . . . . 159
    W. R. S. Garton

III. A COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS FOR THE
     LOWERING OF THE IONIZATION POTENTIAL IN AN EQUILIBRIUM PLASMA . . 173
     H. N. Olsen

IV. A PROPOSED EXPERIMENT TO STUDY THE DEPRESSION OF THE IONIZATION
    POTENTIAL IN A PLASMA . . . . . . . . . . . . . . . . . . . . . . . . . . . . 181
    D. D. Burgess, W. H. Parkinson and E. M. Reeves

V. PROPOSAL FOR AN INVESTIGATION OF HIGHLY EXCITED STATES IN A
    DISCHARGE BY MEANS OF A TUNABLE LASER BEAM . . . . . . . . . . . . . 189
    B. Brehm

SUMMARY OF DISCUSSIONS . . . . . . . . . . . . . . . . . . . . . . . . . . . . 193

LIST OF PARTICIPANTS . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 201

APPENDIX: BIBLIOGRAPHY OF RESEARCH ON LOWERING OF IONIZATION POTENTIALS
    IN PLASMAS . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . A-1
    S. G. Brush and B. H. Armstrong
INTRODUCTION

by

G. Ecker

(Conference Chairman)

The problem of the "Lowering of the Ionization Energy in a Plasma" has been studied for more than thirty years with increasing interest. The reason is that many of our plasmas are partially ionized and to calculate the number of "free" electrons and ions knowledge of the lowering of the ionization energy is required.

Nevertheless our understanding of this problem is far from complete. There is lack of definition of the concepts. Many results are based on intuition or derived from oversimplified models resulting in strongly differing formulas for the lowering of the ionization energy.

We had doubts whether the whole situation was not too confused and the present knowledge too rudimentary to warrant a workshop on the subject. That we came to a positive decision was essentially due to the encouragement by the chairman of JILA, Dr. Branscomb, to whom we are grateful for his support of the idea of this conference and the provision of the means and facilities to make it possible.
To ease the coordination of the following original contributions which elaborate on specific questions I will try to outline here the overall problem and its background in general terms and, - as brief as possible.

It is elementary knowledge that analysis of a system in thermodynamic equilibrium can be carried out if we know the stationary states of the system. This allows the evaluation of the partition function and with that the calculation of all thermodynamic properties. More detailed it provides the expectation value of any quantity which can be defined for the stationary state (e.g. the conductivity) through the ensemble average.

If the task could be solved in such generality the problem of the lowering of the ionization energy would not at all arise and Saha's equation for instance would not even occur in the calculation of a partially ionized gas. However, so far the above procedure is academic.

Instead we find in the literature quite generally the following CRUCIAL APPROXIMATION. It is assumed that the stationary states of the system can be considered as composed of only two independent groups of particle states of the electrons and atomic nuclei: Classically weakly interacting free particle states on the one hand and independent bound states of a small number of individuals on the other hand.

It is this commonly used approximation which causes the introduction of the concept of the lowering of the ionization energy \( \Delta \chi \), the uncertainty of its definition and of its numerical value. Namely, in each stationary state there is a group of particle states which due to free-bound interaction, strong correlations and quantum-mechanical effects cannot really be attributed
to either of the two above groups. This makes the limit between "free" and
"bound" and with that $\Delta \chi$ an uncertain quantity. Moreover whether a
particle is to be termed "free" or "bound" can depend on the effect studied
and different values of $\Delta \chi$ may be expected for different phenomena. Further
the limitation of the atomic partition function $\Delta \chi_p$ and the lowering of
the ionization energy $\Delta \chi$ are different from each other, from the series
limit $\Delta \chi_C$ and from the effective lowering of the ionization energy in the
Saha equation $\Delta \chi_S$.

Serious discrepancies arise if one treats the free and bound states of
the same system as two different independent particle kinds assuming that
the whole phase space is accessible to each of them and that they do not
interact at all. In this case divergencies for the atomic and the free
particle partition function occur and all $\Delta \chi$ are zero.

If one takes into account FREE-FREE INTERACTION neglecting strong
correlations, quantum-mechanical effects and free-bound interaction $\Delta \chi_S$
below the critical density is given by the well-known Debye term. In this
range higher order corrections to the Debye term are very small. Above the
critical density $\Delta \chi$ is given by the so-called "lattice term" varying
with the inverse of the average free particle spacing. These results have
been produced by various authors engaging "Gedankenexperimente" as early
as 1930 and refined cluster expansions more recently. (For a survey of this
literature see for instance the paper by Ecker and Kröll in this issue.)

This account of the free-free interaction does not remove the diver-
gence of the atomic partition function. Within the frame of these
investigations this difficulty is avoided by identifying the limitation
of the atomic partition function $\Delta \chi_p$ with $\Delta \chi_s$, which is unjustified. Also the question of the series limit $\Delta \chi_c$ cannot be answered from the above analysis.

To remove these drawbacks it is necessary to extend the original model through the inclusion of the FREE-BOUND INTERACTION. This free-bound interaction affects the classification into "bound" and "free" states since due to this interaction originally bound states change into a band structure similar to that observed in metals. The shift of the limit between free and bound influences as well $\Delta \chi$ as $\Delta \chi_s$. It also determines the limitation of the atomic partition function, $\Delta \chi_p$. Furthermore free-bound interaction describes the broadening and shift of the energy levels which determines the limit of the series continuum $\Delta \chi_c$ and the shift of the energy levels in the atomic partition function.

Account of the free-bound interaction - particularly for the "highly excited states" - seems to be one of the most urgent requirements for a deeper insight into the problems of a partially ionized plasma in equilibrium. This task is difficult. If it is solved our understanding will be improved and corrections larger than those calculated from higher order correlations of pure free-free interaction can be expected.

Under special conditions still another interaction contribution neglected so far can become important, the BOUND-BOUND INTERACTION. For sufficient high neutral densities their contribution can influence all of those critical quantities discussed above. Fortunately in most of the practical applications this effect is small. However, experiments under
extremely high pressures have already produced values of the "lowering of the ionization energy" which can only be understood on the basis of such bound-bound interactions.
I. PROBLEMS OF THE PLASMA IN EQUILIBRIUM

by

G. Ecker and W. Kröll


The plasma in thermodynamic equilibrium has been extensively discussed on the basis of the assumption that all particles can be classified as "bound" or "free." Under this assumption simple models led to divergencies of the partition functions of bound and free particles as well as to discrepancies of the predicted level shift and lowering of the ionization potential. On the basis of a quantum-mechanical treatment we develop a "free-bound-approximation" for the eigenstates and a classical approximation for the partition function. It is a decisive feature of the analysis that it takes free-bound interaction into account. The results remove the divergence difficulties and produce values for the "lowering of the ionization potential" and the limit of the "series-continuum."
SYSTEM

Subject of this investigation is a system of equal numbers of electrons and protons in thermodynamic equilibrium at a given temperature and volume below the critical density. Both, electrons and protons are represented by point charges interacting according to Coulomb's law. The formation of hydrogen atoms is taken into account but not the effects of negative ions or molecules. No external influences and boundary effects are considered.

The model of a hydrogen plasma has been chosen for the sake of formal simplicity. For other plasmas the problems are similar and our procedure is readily applied.

THE PROBLEMS

The analysis of the described system demands the solution of a quantum mechanical many-body problem. To avoid the formidable difficulties of this solution simplifying models have been introduced. Shortcomings of these models led to the following problems:

DIVERGENCE OF THE ATOMIC PARTITION FUNCTION

DISCREPANCIES IN THE CALCULATED EFFECT OF LEVEL SHIFT AND BROADENING ON THE ATOMIC PARTITION FUNCTION

DIVERGENCES OF THE CLASSICAL PARTITION FUNCTION OF FREE ELECTRONS AND PROTONS

DISCREPANCIES IN THE LOWERING OF THE IONIZATION POTENTIAL

These problems are not independent, but neither can they be identified with one another as has been done occasionally in the past.
PREVIOUS RESULTS

DIVERGENCE OF THE ATOMIC PARTITION FUNCTION. Attempts to limit the hydrogen partition function have been based on very different models and date back as early as 1916.

It has been argued that eigenstates with an extension larger than the plasma volume cannot exist. A much stronger limitation was introduced by the omission of eigenstates extending beyond the next neutral neighbour. If the influence of the nearest ionic neighbour is assumed to dominate, then only eigenstates with an energy $\varepsilon_b < - \frac{3e^2}{r_0}$ contribute to the partition function ($r_0$ - average interionic distance). This result was derived from the assumption that bound states do not exist if their energy exceeds the potential energy maximum between two ions in the average distance.

The simultaneous average interaction of the electrons and ions can be taken into account by solving the Schrödinger equation with the Debye potential. As was pointed out (l.c.) this procedure is valid for the highly excited states only and yields an upper limit $\varepsilon_b < - \frac{e^2}{D}$ for the eigenstates ($D$ - Debye length). Essentially the same result has been derived on the basis of a perturbation theory and under the assumption that the atomic electron experiences a constant potential shift due to the free particles.

BROADENING AND LEVEL SHIFT. In this section shift and broadening of the eigenstates are considered only to the extent that they affect the series-limit and the partition function.

Atomic eigenstates contribute to the continuum if the broadening of their energy levels is of the same order of magnitude as the separa-
tion of consecutive terms. Using this concept it was stated that all levels with

\[ \mathcal{E}_n > -\frac{e^2}{r_0} \left( \frac{r_0}{a_0} \right)^{1/5} \]

merge in the continuum \(^{10}\) (\(a_0\) - Bohr radius).

In principle a shift is experienced by all energy levels. It has been claimed that for the low energy states this shift influences the partition function only negligibly.\(^ {11}\) In contrast the application of the Schrödinger equation with the Debye potential to the low levels \(^ {12}\) yielded a ground state shift of the order \(-\frac{e^2}{D}\).

A recent investigation \(^ {13}\) calculates the shift and broadening of the energy levels including nonstationary effects within the limitations of the random phase approximation. It produces an approximate description of the electron collision broadening and a small upward shift varying with the inverse square of the principal quantum number.

**DIVERGENCE OF THE CLASSICAL PARTITION FUNCTION.** Obviously the classical partition function of the electrons and protons exhibits an essential divergence due to the short range interaction of oppositely charged particles. In the limit of very high temperatures an effective short range potential removing the divergence was calculated from quantum mechanics.\(^ {14}\) A purely classical investigation restricts the partition function to positive values of the electron-ion pair energy in order to secure convergence.\(^ {15}\) The divergence discussed here is to be distinguished from the short and the long range divergence occurring in the cluster expansions for Coulomb systems. The latter one was removed by the introduction of the Prototype Cluster Expansion.\(^ {16}\) The short range divergence caused by this Prototype Expansion was eliminated by the Giant Cluster Concept.\(^ {17}\)
LOWERING OF THE IONIZATION ENERGY. Unsöld's concept together with the usual definition of the ionization energy as the energy difference between the bound and the lowest free state provides for the lowering of the ionization energy the value $\Delta_0 \chi = e^2 / r_0$.

The term $\Delta_1 \chi = e^2 / D$ for the lowering of the ionization energy in the Saha equation has been calculated as the contribution of the free particle Coulomb interaction to the chemical potential. $^{18, 19, 11, 20}$

A stronger lowering of the ionization potential follows from the formula $^{7}$ $\Delta_2 \chi = e^2 / D + \mathcal{L} e^2 / r_0$ where the second term was added in analogy to metal theory to take into account the contributions of overlapping high energy bound states ($\mathcal{O}(\mathcal{L}) = 1$). The investigations $^{19, 11}$ restrict the term $\Delta_1 \chi = e^2 / D$ to the range below and the term $\Delta_0 \chi = e^2 / r_0$ to the range above the critical density $n_c \approx (3/4 \pi) \cdot (KT/e^2)^3$. Other investigations claim that the terms $\Delta_0 \chi$ and $\Delta_2 \chi$ should be added. $^{21, 22}$

It has been expected that the value of the lowering of the ionization energy depends on the thermodynamical potential used for the derivation of the Saha equation. $^{23}$

IDENTIFICATION OF THE LIMITS. In the literature the cut-off for the atomic partition function, the depression of the continuum and the lowering of the ionization energy in the Saha equation have been identified with each other. $^{21-26}$ However, the necessity to distinguish between these quantities was also pointed out. $^7$

CLASSIFICATION AND TERMINOLOGY

It will prove suitable to classify all particles of the system in the following energy scale (E-scale):

A particle is labeled with $E$, if the value of its
pair energy with the nearest oppositely charged neighbour in their center of gravity system is $\xi$, neglecting all other interactions.

We distinguish two particle groups: free particles ($f$) and bound particles ($b$).

In the free group we specify the subgroup of quasi-free states ($qf$) which are influenced by strong-correlations and quantum-mechanical effects, whereas the other free states can be described classically with weak pair correlations.

In the bound group we specify the bound-hydrogen-like ($h$) states, which can be approximately described in terms of hydrogen functions, whereas this is not possible for the rest of the bound states.

The limits between these particle groups in the $\xi$-scale are $\xi_h$, $\xi_b$ and $\xi_f$ as shown in fig. 1.

AIM OF THIS INVESTIGATION

All the investigations quoted in the previous section use the approximation that all particles can be classified in two groups - free particles and bound particles.

Within this classification the lack of understanding and the discrepancies indicated above are in our opinion due to the use of different incomplete models of a rather elementary nature.

It is our aim to contribute to the resolution of these difficulties by a systematical quantum-mechanical treatment of the canonical partition function and of the free-bound-approximation which is defined in the following section.
In doing so we stay within the frame of the classification in free and bound particles since it describes the large majority of the particles correctly and is adapted to the discussion of the problems states above. We are well aware that there are particles which do not exactly fit in any of these two groups.

We will see that we can reach our aim by answering four questions concerning the particle states of the "free-bound model":

I. Up to what limit \( (e_h) \) in the energy scale of the isolated electron-ion pair is the concept of bound states applicable in the plasma?

II. Up to what limit \( (e_h) \) in the energy scale of the isolated electron-ion pair can the bound states be considered hydrogenlike?

III. To what extent is the partition function of our system open to a classical treatment?

IV. How large is the lowering of the ionization energy?

**ADAPTED FREE-BOUND APPROXIMATION**

**DEFINITION:** In accord with the general use in the literature the adapted free-bound model admits only two types of particle states - free and bound ones. However, in contrast to the naive free-bound limit \( e = 0 \) it applies the following definition of free and bound:

Consider the particle 1 and the quantity

\[
G_{1\nu} = \int \psi \psi^* |r_1 - r_\nu| dV
\]

where the index \( \nu \) designates one of the oppositely charged particles,
ψ is the eigenfunction for a given stationary state of the whole system and the integral is to be extended over the Ï„-space. Then particle 1 is considered bound if there exists a \( k \) with

\[
C_{1k} \ll C_{1\nu} \quad \text{for all } \nu \neq k
\]

Particle 1 is considered to be free if such a \( k \) does not exist.

Physically this means that a particle 1 is bound if it is found preferentially in the near environment of one ion \( k \). It is free if there is no preference for one certain ion only.

With respect to the definitions of quasi-free and bound-hydrogen-like particles we refer to the paragraph "classification and terminology."

**ANALYSIS:** The eigenfunctions \( \psi \) and eigenvalues \( E \) of our system are determined by the equation

\[
\hat{H}\psi_m = E_m\psi_m
\]

(1)

where \( \hat{H} \) denotes the Hamiltonian operator of the whole system and \( m \) represents the set of the discrete, \( \mathcal{P} \) the continuous quantum numbers.

From this equation (1) we want to derive by a perturbation procedure quantitative criteria for the above defined concepts of free, bound and bound-hydrogen-like.

In the zero order we compose the eigenfunction of a stationary plasma of two groups of independent single - (I) and two particle (II) eigenfunctions. The single particle functions are planar waves, the two particle functions are the product of a hydrogen eigenfunction for the relative - and a planar wave for the center of gravity coordinate.

The criterion whether in the zero order the state of a particle belongs to group (I) or (II) is the "naive" concept of free and bound: A particle is free or bound depending on whether its \( \epsilon \)-value is positive or negative.
The zero order eigenfunction is then

\[ \psi^{(0)} = \left[ \frac{1}{(N!)^2} \sum_{j} (-1)^j \left\{ \prod_{i} \frac{i}{\hbar} p_i r_i \right\} \prod_{j} \phi_j (\xi_j) \right] m_\beta \]

(2)

where \( \xi_j \) and \( R_j \) are the relative and center of gravity coordinate of the bound state \( (1) \). \( r_i \) and \( p_i \) are resp. the coordinates and momenta of the free particles, \( \phi_j \) is the hydrogen eigenfunction with the quantum number \( \nu_{\ell m} \) and the eigenvalue \( \mathcal{E}_\ell \), \( N \) is the total number of electrons or ions. \( \mathcal{P}_j \) is the set of permutation operators covering all exchanges between all identical particles. \( |\mathcal{P}_j| \) denotes the number of corresponding transpositions.

For simplicity we omit in the following the indices of the total eigenstate \( (m_\beta) \), wherever it can be done without ambiguity. Also we neglect effects due to exchange degeneracy using only one of the permutation terms in eq. (2). The formally complicated evaluation including all terms of eq. (2) has been carried through. As to be expected this yields the same result provided that the matrix elements of the perturbation operator with different permutation terms of eq. (2) are negligible.

In accord with our zero order eigenfunction we subdivide the Hamilton operator in

\[ \hat{\mathcal{H}} = \hat{\mathcal{H}}_I + \hat{\mathcal{H}}_{II} + \hat{\mathcal{H}}^* \]

(3)

with

\[ \hat{\mathcal{H}}_I = -\frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{\Delta_i}{m_i} \]

(4)
\[ \hat{H}_{\text{II}} = \sum_{\ell \neq k} \hat{H}_{\ell k} = \sum_{\ell \neq k} \left\{ -\frac{\ell^2}{2} \left( \frac{\Delta_{k+}}{m_+} + \frac{\Delta_{k-}}{m_-} \right) - \frac{e^2}{|r_{k+} - r_{k-}|} \right\} \]  

\[ \hat{H} = \sum_{\ell} \hat{V}_{\ell I} + \frac{1}{2} \sum_{\ell, k} \hat{V}_{\ell k} + \frac{1}{2} \sum_{i, j} V_{ij} \quad V_{ij} = e \sum_{\ell} \left( \frac{e_i}{|r_{k+} - r_i|} - \frac{e_i}{|r_{k-} - r_i|} \right) \]

\[ + \frac{e}{2} \sum_{\ell} \left( \frac{1}{|r_{k+} - r_{k+}|} - \frac{1}{|r_{k-} - r_{k+}|} - \frac{1}{|r_{k+} - r_{k-}|} + \frac{1}{|r_{k-} - r_{k-}|} \right) \]

\[ + \frac{1}{2} \sum_{i, j} \frac{e_i e_j}{|r_i - r_j|} \]

where the indices \( l_+ \) and \( l_- \) characterize the ion and the electron in the \( l \)th bound state.

The zero order energy of the system is given by

\[ E(0) = \sum_{i} \frac{p_i^2}{2m_i} + \sum_{\ell} \epsilon_{\ell} + \sum_{\ell} \frac{P_{\ell}^2}{2M} \]

with \( M = m_+ + m_- \).

The first order perturbation is governed by the equation

\[ (\hat{H}_I + \hat{H}_{\text{II}}) \psi(1) - E(0) \psi(1) = -\sum_{\ell} \hat{V}_{\ell I} \psi(0) - \frac{1}{2} \sum_{\ell, k} V_{\ell k} \psi(0) \]

\[ - \frac{1}{2} \sum_{i, j} V_{ij} \psi(0) \]
We use

\[ E^{(1)} = \sum_{k} E_{k}^{(1)} + E_{I}^{(1)} + E_{II}^{(1)} \]  (9)

where the energy \( E_{k}^{(1)} \) is the perturbation energy due to the interaction of the pair \((1,1)\) with all particles of group I, whereas \( E_{I}^{(1)} \) and \( E_{II}^{(1)} \) account for the interaction within the groups I and II respectively.

Up to the first order we represent the eigenfunctions in the form

\[ \Psi = \Psi^{(0)} + \sum_{k} \Psi_{k}^{(1)} + \Psi_{I}^{(1)} + \Psi_{II}^{(1)} \]  (10)

where \( \Psi_{k}^{(1)} \), \( \Psi_{I}^{(1)} \) and \( \Psi_{II}^{(1)} \) satisfy the equations

\[ (\hat{H}_{I} + \hat{H}_{II}) \Psi_{k}^{(1)} - E^{(0)} \Psi_{k}^{(1)} = -\sum_{l} V_{kl} \Psi_{l}^{(0)} - \frac{1}{2} \sum_{l,k} V_{lk} \Psi_{l}^{(0)} + E_{I}^{(1)} \Psi_{l}^{(0)} \]  (11)

and

\[ (\hat{H}_{I} + \hat{H}_{II}) \Psi_{I}^{(1)} - E^{(0)} \Psi_{I}^{(1)} = -\frac{1}{2} \sum_{i,j} V_{ij} \Psi_{i}^{(0)} + E_{I}^{(1)} \Psi_{i}^{(0)} \]  (12)

\[ (\hat{H}_{I} + \hat{H}_{II}) \Psi_{II}^{(1)} - E^{(0)} \Psi_{II}^{(1)} = -\frac{1}{2} \sum_{l,k} V_{lk} \Psi_{l}^{(0)} + E_{II}^{(1)} \Psi_{l}^{(0)} \]  (13)

We consider the contribution \( \Psi_{k}^{(1)} \) which describes the change of the eigenfunction due to the interaction of the pair \((1,1)\) with the "free" particles of group I. We use the development

\[ \Psi_{k}^{(1)} = \sum_{s} \int_{sP'} \Psi_{sP'}^{(0)} \, dp' \]  (14)
where the symbol $\mathcal{P}$ stands as well for the set of continuous quantum numbers (p) of the free particles as for the parameters (P) describing the translation of the pairs of group II.

Using the relation

\[ \int \psi^{(0)^*} \psi^{(0)} \frac{1}{xp'} \frac{1}{mp} \, dr = \delta(p - p') \delta_{ms} \]  \hspace{1cm} (15)

the coefficient $a_{sp'}$ follows from (11) to be

\[ a_{sp'} = \frac{E_{x1}^{(1)} \delta(p - p') \delta_{ms} - V_{sm'p'}}{E_s^{(0)} - E_m^{(0)}} \]  \hspace{1cm} (16)

with

\[ V_{sm'p'} = \int \psi^{(0)^*} \psi^{(0)} \frac{1}{sp'} \frac{1}{xm'} \, dr \]  \hspace{1cm} (17)

According to the perturbation theory of continuous systems\(^{27}\) this requires $E_{1}^{(1)} = 0$ and we have therefore

\[ \psi_{x1}^{(1)} = - \sum_{s} \int \frac{V_{sm'p'}}{E_s^{(0)} - E_m^{(0)}} \psi^{(0)} \, dp' \]  \hspace{1cm} (18)

Using $V_{11}$ from eq. (6) we have

\[ V_{sm'p'} = \sum_{i} e_i \int \psi^{(0)^*} \left( \frac{1}{|r_{x+} - r_i|} - \frac{1}{|r_{x-} - r_i|} \right) \psi^{(0)} \, dp' \]  \hspace{1cm} (19)

Introducing eq. (2) into (19) and using at the same time the orthogonality and normalization relation (15) we find that the sum (19) consists of two different types of terms.
\[ V_{k,i} = e e_{i} \Pi \delta(p_j' - p_j) \delta(P_{\sigma}' - P_{\sigma}) \Pi \delta_{\nu_{ks} \nu_{km}} \]

\[ \times \int \frac{1}{\hbar} \left( \frac{1}{|r_{k+} - r_i|} - \frac{1}{|r_{k-} - r_i|} \right) \phi_{\nu_{ks}}(\xi_{k}) \phi_{\nu_{km}}(\xi_{k}) \]

\[ \times \frac{dr_i \, dR_k \, d\xi_k}{\hbar^6} \]

and

\[ V_{k,i} = e e_{i} \Pi \delta(p_j' - p_j) \delta(P_{\sigma}' - P_{\sigma}) \Pi \delta_{\nu_{ks} \nu_{km}} \]

\[ \times \int \frac{1}{\hbar} \left( \frac{1}{|r_{k+} - r_i|} - \frac{1}{|r_{k-} - r_i|} \right) \phi_{\nu_{is}}(\xi_{i}) \phi_{\nu_{km}}(\xi_{k}) \]

\[ \times \frac{dr_i \, dR_k \, d\xi_k}{\hbar^6} \]

Let us first consider the terms \( V_{1,i} \). We develop \( V_{1,i} \) in a power series with respect to \( \xi_k \) and restrict ourselves to the first order term

\[ V_{1,i} = e e_{i} \frac{(R_k - r_i) \xi_k}{|R_k - r_i|^3} \]

The justification for this procedure is given below.

Introducing eq. (22) into eq. (19) using the abbreviations

\[ D_{j\sigma} = \Pi \delta(p_j' - p_j) \delta(P_{\sigma}' - P_{\sigma}) \]

\[ \Delta P_i = p_{i}' - p_i \]

\[ \Delta P_k = P_k' - P_k \]
we obtain

\[ \bar{\nu}_{j,i} = D_{j0} \text{ee} \langle \nu_{ls} | \xi | \nu_{lm} \rangle \int \frac{(R_j - r_i)}{|R_j - r_i|^3} e^{-\frac{i}{\hbar} (r_i \Delta P_i + R_j \Delta P_j)} \frac{dr_i \, dR_j}{h^6} \]

where \( \langle \nu_{ls} | \xi | \nu_{lm} \rangle \) is the quantum mechanical dipole moment.

The evaluation of the integral produces

\[ \bar{\nu}_{j,i} = \text{ie} e \frac{D_{j0}}{\hbar^3} 4\pi \langle \nu_{ls} | \xi | \nu_{lm} \rangle \cos \theta_1 \delta(\Delta P_j + \Delta P_i) \frac{\hbar}{|\Delta P_i|} \]

where \( \theta_1 \) is the angle between \( \langle \nu_{ls} | \xi | \nu_{lm} \rangle \) and \( \Delta P_i \). Introducing eq. (25) into eq. (18) we find

\[ \bar{\nu}_{jI}^{(1)} = \text{ie} \sum_s \sum_i e_i 4\pi \langle \nu_{ls} | \xi | \nu_{lm} \rangle \frac{\hbar}{\hbar^3} \frac{\psi^{(0)}_{m\rho}}{\phi_{\nu_{ls}}} \phi_{\nu_{lm}} \times \int \frac{\Delta P_i (r_i - R_j)}{|\Delta P_i| \{\Delta \varepsilon + \Delta P_i \cdot v_r + |\Delta P_i|^2 / 2\mu\}} \cos \theta_1 \delta(\Delta P_i) \]

Here \( \Delta \varepsilon \) is the change in the excitational energy and the abbreviations

\[ v_r = \frac{P_i}{m_i} - \frac{P_j}{M} \quad \text{and} \quad \frac{1}{\mu} = \frac{1}{m_i} + \frac{1}{M} \]

are used.

An exact evaluation of this integral is extremely involved and beyond the scope of this paper. A crude approximation sufficient for our order of magnitude estimate can be obtained for a perturbing electron as well as for a perturbing ion in the range
\[ r_0 = \left( \frac{3\sqrt[3]{2}}{4\pi\hbar^2} \right) \frac{1}{\lambda} \Rightarrow r_w = \frac{\alpha^2}{kT} \Rightarrow \lambda = \frac{1}{\sqrt{2\pi\mu kT}} \tag{28} \]

observing that the principal value has to be taken where the denominator causes a divergence.

Within the range of our assumption of weak pair correlations the first inequality of eq. (28) is always fulfilled. The second inequality is satisfied up to temperatures of about a million degrees.

It is found that in the range \( \Delta \epsilon \gg kT \) electrons and ions have the same perturbation effect described by

\[ \frac{\psi^{(1)}_{\ell I}}{\psi^{(0)}_{\ell I}} = \frac{\phi_{\ell I} \left( x \right)}{\phi_{\ell I} \left( \xi \right)} e^{\frac{\epsilon^2}{r_0^2}} \left\langle v_{\ell I} \mid \xi \mid v_{\ell I} \right\rangle \frac{1}{\Delta \epsilon} \tag{29} \]

In the range \( \Delta \epsilon \ll kT \) however, the contribution of the electrons dominates that of the ions and results in

\[ \frac{\psi^{(1)}_{\ell I}}{\psi^{(0)}_{\ell I}} = \frac{\phi_{\ell I} \left( x \right)}{\phi_{\ell I} \left( \xi \right)} e^{\frac{\epsilon^2}{r_0^2}} \left\langle v_{\ell I} \mid \xi \mid v_{\ell I} \right\rangle \frac{1}{\sqrt{\Delta \epsilon \cdot kT}} \tag{30} \]

In eqs. (29) and (30) we have represented the sum over all \( (i, s) \) by its average maximum value. In this sense here and in the following \( \Delta \epsilon \) denotes the transition to the next neighbouring state.

Let us now consider the terms \( \widetilde{V}_{l, i} \) where the index \( (i) \) denotes a perturbing ion.\(^\dagger\) We must first express the quantities \( r_{1+} \), \( r_{1-} \), \( \alpha \) and \( R_i \) in eq. (21) in terms of \( \tilde{\xi}_l \), \( R_1 \) and \( r_i \) by the relations

\[^\dagger\] An estimate of the corresponding term with a perturbing electron shows that the ion term considered here is representative.
\[ r_{\pm} = R_{\pm} - \frac{m}{M} \xi_{\pm}; \quad r_{\pm} = R_{\pm} + \frac{m^+}{M} \xi_{\pm} \quad \xi_{\pm} = \frac{m^+}{M} \xi_{\pm} + R_{\pm} - r_{\pm} \]

\[ R_{\pm} = \frac{m^+}{\lambda} r_{\pm} - \frac{m^-}{M} R_{\pm} + \frac{m^+ m^-}{M^2} \xi_{\pm} \]

Introducing further the variables \( \eta_1, \eta_2 \) by

\[ r_{\pm} = \frac{\eta_1 + \eta_2}{2} \quad \quad R_{\pm} = \frac{\eta_1 - \eta_2}{2} \]

and performing the integration over \( \eta_1 \) we arrive at

\[ \hat{\psi}_{k, i} = \frac{D\sigma_{i0}}{h^3} \delta(p_1 + p_\pm - p'_1 - p'_\pm) \int \frac{i}{\pi} (\Lambda_1 \xi_{\pm} + \Lambda_2 \eta_2) \phi^{*}_{\nu i s}(\xi_{\pm}) \]

\[ \times \left( \frac{1}{|\eta_2 - \frac{m}{M} \xi_{\pm}|} - \frac{1}{|\eta_2 + \frac{m^+}{M} \xi_{\pm}|} \right) \phi_{\nu k m}(\xi_{\pm}) \frac{d\xi_{\pm} d\eta_2}{h^3} \]

with

\[ \Lambda_1 = \frac{m}{M} (p'_\pm - \frac{m^+}{M} p'_1) \quad \quad \Lambda_2 = \frac{1}{2} (p'_\pm + p'_1 - p_{\pm} - \left( \frac{m^+ - m^-}{M} \right) p'_1) \]

Using eqs. (33) and (34) in eq. (18) and carrying out the integrations with respect to \( D\sigma_{i0} \) we find
\[ \hat{\psi}^{(1)}_{\lambda \lambda} = \sum_i \sum_s e^i e^s \psi^{(0)} \left[ \phi_{\nu_is} (\xi_i) \phi_{\nu_is} (\xi_s) \int \frac{1}{\Delta \xi + \frac{2}{2M} + \frac{2}{2m_+}} e^{i \left( \frac{1}{\hbar} \Delta \xi \Delta \xi - \frac{1}{\hbar} \Delta \xi \Delta m \right)} d\xi_1 d\eta_2 \right] \times \left[ \frac{1}{|\Delta r|} - \frac{1}{|\Delta r + \xi_1|} \right] \frac{d(\Delta \xi)}{\hbar^3} \right] (35) \]

where it should be remembered that in \( \hat{\psi}_{\nu_is} (\xi_i) \) the coordinate \( \xi_i \) should be expressed by \( \xi_1, R_1 \) and \( r_i \) as given in eq. (31).

We evaluate eq. (35) in the same approximation as eq. (26). Performing the integration with respect to \( P_i \) eliminating at the same time \( r_1+ \) and \( R_i \) using the eqs. (31) we obtain

\[ \hat{\psi}^{(1)}_{\lambda \lambda} = \sum_i \sum_s e^i e^s \psi^{(0)} \left[ \phi_{\nu_is} (\xi_i) \phi_{\nu_is} (\xi_s) \int e^{i \left( \frac{1}{\hbar} \Delta \xi \Delta \eta \right)} \phi_{\nu_is}^{*} (\xi_i) \phi_{\nu_is} (\xi_s) \right] \times \left[ \frac{1}{|\Delta r|} - \frac{1}{|\Delta r + \xi_1|} \right] \frac{d(\Delta \xi)}{\hbar^3} \right] \]

where we have neglected terms of the order \( m_-/m_+ \) and applied the abbreviation \( \Delta p_1 = p_1 - P_1 \). Integrating first with respect to \( \Delta p_1 \) and then over \( \nu_2 \) we finally have

\[ \hat{\psi}^{(1)}_{\lambda \lambda} = \sum_i \sum_s e^i e^s \psi^{(0)} \left[ \phi_{\nu_is} (\xi_i) \phi_{\nu_is} (\xi_s) \int \phi_{\nu_is}^{*} (\xi_i - \Delta r) \phi_{\nu_is} (\xi_s - \Delta r) \right] \times \left[ \frac{1}{|\Delta r|} - \frac{1}{|\Delta r + \xi_1|} \right] d\xi_1 \]
The total effect of the free-bound interaction on the eigenfunctions represents itself as the sum over the contributions of the type \( \psi^{(4)}_\lambda \) and \( \psi^{(4)}_{\pi} \) given in eqs. (29), (30) and (37), respectively.

The perturbations \( \psi^{(4)}_\lambda \) and \( \psi^{(4)}_{\pi} \) due to bound-bound and free-free interactions are not considered in this paper. The reason is that the bound-bound interaction becomes important only for extreme gas densities. This is supported by experimental evidence from gases compressed isentropically up to pressures of \( 10^4 \) atmospheres. The contribution \( \psi^{(4)}_{\pi} \) is not treated here since its result is well-known, at least as far as it accounts for weak pair correlation.

Neglecting consequently \( \psi^{(4)}_\lambda \) and \( \psi^{(4)}_{\pi} \) the eigenfunction up to first order follows from eqs. (29), (30) and (37) to be

\[
\psi = \psi^{(0)}_I \prod \frac{\phi_{v_\lambda}(\xi_\lambda)}{\xi_\lambda} - \frac{e^2}{\pi_0} \left\langle \nu_\lambda | \xi_\lambda | \nu_\lambda + 1 \right\rangle x_{v_\lambda} \phi_{v_\lambda + 1}(\xi_\lambda)
\]

\[
+ \sum_s \sum_i \left\{ \frac{e_{\epsilon_\lambda}}{\Delta \epsilon_{v_\lambda}} \phi_{v_\lambda}(\xi_\lambda - \Delta r) \phi_{v_\lambda}(\xi_\lambda) \left[ \frac{1}{\Delta r} - \frac{1}{\Delta r + \xi_\lambda} \right] d\xi_\lambda \right\} \phi_{v_\lambda}(\xi_\lambda)
\]

where \( X_{v_\lambda} \) is \( \Delta \epsilon_{v_\lambda} \) or \( \frac{\sqrt{\Delta \epsilon_{v_\lambda} k^4}}{k} \) depending on whether \( \epsilon_{v_\lambda} \) is larger or smaller than \( kT \).

So far we have not taken into account degeneracy. This is done by replacing throughout eq. (38) the zero order eigenfunctions by those adapted to the perturbation.

In our problem two types of degeneracy are important: First the usual degeneracy within one hydrogen level. Second the "resonance degeneracy" of equivalent states of the bound and the perturbing ion.
We designate the adapted eigenfunction within the hydrogen level by \( \tilde{\phi} \). Then due to the resonance degeneracy the zero order eigenfunction is composed of terms of the form

\[
\psi_{k,i}^{(0)} = c_{k} \, \tilde{\psi}_{v}(\xi_{k}) + c_{i} \, \tilde{\psi}_{v}(\xi_{i})
\]

where \( c_{1} \) and \( c_{2} \) are given by

\[
c_{k} = \left( \frac{V_{ki}}{2 |V_{ki}|} \left[ 1 + \frac{V_{kk} - V_{ii}}{\sqrt{(V_{kk} - V_{ii})^2 + 4 |V_{ki}|^2}} \right] \right)^{1/2} \tag{40}
\]

\[
c_{i} = \left( \frac{V_{ki}}{2 |V_{ki}|} \left[ 1 + \frac{V_{kk} - V_{ii}}{\sqrt{(V_{kk} - V_{ii})^2 + 4 |V_{ki}|^2}} \right] \right)^{1/2} \tag{41}
\]

with \(^\dagger\)

\[
V_{kk} = e^{2} \int \tilde{\psi}_{v}^{*}(\xi_{k}) \, \tilde{\psi}_{v}(\xi_{k}) \, \frac{1}{|\xi_{k} + R_{k} - y_{i}|} \, d\xi_{k} \tag{42}
\]

\[
V_{ii} = e^{2} \int \tilde{\psi}_{v}^{*}(\xi_{i}) \, \tilde{\psi}_{v}(\xi_{i}) \, \frac{1}{|\xi_{i}|} \, d\xi_{i} \tag{43}
\]

\[
V_{ki} = e^{2} \int \tilde{\psi}_{v}^{*}(\xi_{k}) \, \tilde{\psi}_{v}(\xi_{k} + R_{k} - r_{i}) \, \frac{1}{|\xi_{k} + R_{k} - r_{i}|} \, d\xi_{k} \tag{44}
\]

\(\dagger\)The quasi-static treatment of the exchange degeneracy effects is justified within the range of our condition (28).
Using the definitions from page 5-7, eq. (39) to (44) provide for the "free-bound limit" \((\mathcal{E}_\Delta)\) the criterion

\[ V_{\perp \perp} = V_{\parallel \parallel} \]  \hspace{1cm} (45)

For the "hydrogenlike limit" \((\mathcal{E}_h)\) follows from eq. (38)

\[ \frac{e^2}{r_0^2} \left\langle n_h \left| \mathcal{E} \right| n_h \right\rangle \frac{1}{\sqrt{\Delta \mathcal{E}_h \cdot KT}} = 1 \]  \hspace{1cm} (46)

since it is readily shown that in the range below the critical density \(\Delta \mathcal{E}_h \ll KT\) always holds.

We emphasize that the above distinction of free and bound states is different from the commonly used one which employs the "naive" free-bound concept of an isolated electron-ion pair.

CLASSICAL APPROXIMATION TO THE PARTITION FUNCTION

In this paragraph - in contrast to the general use in this paper - we consider a system with fixed numbers of bound and free particles.

The quantum mechanical partition function is given by

\[ Q = \text{tr} \ e^{-\beta H} \]  \hspace{1cm} (47)

where \(H\) is the matrix of the Hamiltonian operator of our system and \(\beta = (KT)^{-1}\).

If we neglect the interaction between the above defined groups of
free and bound particles the Hamiltonian operator $\hat{H}$ is separable into two independent parts $\hat{H}_f$ and $\hat{H}_b$. Under these circumstances $Q$ can be factorized in the form

$$Q = Q_f Q_b = \text{tr} e^{-\beta \hat{H}_f} \text{tr} e^{-\beta \hat{H}_b}$$

(48)

Applying the eigenfunctions of $\hat{H}_b$ in the calculation of $Q_b$ we arrive at

$$Q_b = \frac{1}{N_b} \left[ \left( \frac{2\pi \hbar kT}{\hbar^2} \right)^{3/2} \sum_n e^{-\beta \varepsilon_n} \right]^{N_b}$$

(49)

where $N_b$ is the number of bound particles, $\varepsilon_n$ are the energy eigenvalues of the bound states and the sum includes all degenerate levels.

To calculate $Q_f$ we use the momentum eigenfunctions and obtain

$$Q_f = \frac{1}{6N_f} \frac{1}{(N_f !)^2 \hbar} \int e^{-\frac{i}{\hbar} \sum p_i r_i} e^{-\beta H_f} \frac{i}{\hbar} \sum p_i \int dp dr$$

(50)

where $\int d\vec{r}$ is the volume of the phase space occupied by all free states and $N_f$ the number of free electrons. The term $(N_f !)^2$ is due to the exchange degeneracy. In principle this phenomenon produces additional off-diagonal terms in (50), which are small as follows from the results in the investigations 29, 30, 31 and 14.

Note that a substantial part of the interaction between the naively defined free and bound particle groups is already taken care of by our new definition of free and bound. Therefore the above neglect is here much more justified than in the frame of the naive definition.
Aiming to calculate the function

\[ u = \mathrm{e}^{-\beta H_f} \mathrm{e}^{\frac{1}{\hbar} \sum \frac{p_i r_i}{m_i}} \mathrm{e}^{-\beta H_f} \zeta \]  

we want to solve Bloch's equation

\[ \hat{H}_f u + \frac{\partial u}{\partial \beta} = 0 \]  

through the Ansatz

\[ u = \omega \mathrm{e}^{-\beta H} \zeta \]  

where \( H \) is the classical Hamilton function.

For \( \omega \) follows the differential equation

\[ -\hbar^2 \sum_i \frac{\Delta_i}{m_i} (\zeta \omega \mathrm{e}^{-\beta V}) - w \zeta E_{\text{kin}} \mathrm{e}^{-\beta V} + \zeta \omega \mathrm{e}^{-\beta V} \frac{\partial \omega}{\partial \beta} = 0 \]  

where \( V \) is the potential energy of the free particles.

Eq. (54) may be simplified to

\[ \frac{\partial \omega}{\partial \beta} - \beta V \left\{ \mathrm{i} \hbar \sum_i \frac{p_i}{m_i} v_i (\mathrm{e}^{-\beta V} \omega) + \frac{\hbar^2}{2} \sum_i \frac{\Delta_i}{m_i} (\mathrm{e}^{-\beta V} \omega) \right\} = 0 \]

using

\[ \frac{-\hbar^2}{2} \sum_i \frac{\Delta_i \zeta}{m_i} = \sum_i \frac{p_i^2}{2m_i} \zeta \approx E_{\text{kin}} \zeta \]  

The uncertainty of this approximation caused by quantum-mechanical effects is notable only for very small momenta.
With the boundary condition

$$\lim_{\beta \to +\infty} w = 1$$  \hspace{1cm} (57)$$

eqq. (55) \text{ is readily transformed into the integral equation}

$$w = 1 + \frac{i\pi}{2} \int_0^\beta e^{\nu t} \left\{ \sum_{i} \left( \frac{p_i}{m_i} \right) v_i (e^{-\nu t} w) \right\} dt + \frac{\hbar^2}{2} \int_0^\beta e^{\nu t} \left\{ \sum_{i} \left( \frac{\Delta_i}{m_i} \right) (e^{-\nu t} w) \right\} dt$$  \hspace{1cm} (58)

If we look for solutions of the form

$$w = \sum_{k=0}^{\infty} \hbar^k w_k$$  \hspace{1cm} (59)$$

iteration produces the recursion formula

$$w_0 = 1 \hspace{1cm} w_1 = -\frac{i\pi^2}{2} \sum_{i} \left( \frac{p_i}{m_i} \right) v_i v$$

$$w_k = \int_0^\beta e^{\nu t} \left[ \frac{1}{2} \sum_{i} \left( \frac{\Delta_i}{m_i} \right) (e^{-\nu t} w_{k-2}) + i \sum_{i} \left( \frac{p_i}{m_i} \right) v_i (e^{-\nu t} w_{k-1}) \right] dt$$  \hspace{1cm} (60)

Therefore $Q_f$ is given by

$$Q_f = \int_{r_f} e^{-\beta H} \sum_{k} \hbar^k w_k dr dp$$  \hspace{1cm} (61)$$

In principle the derivation of this result follows a procedure developed by Kirkwood[29].

To decide on the possibilities of a classical approximation to the
partition function (61) we consider the integrand in the two ranges
\[ r^2 \geq r_w \lambda. \]

For \( r^2 > \lambda r_w \) the condition
\[ \left\| \sum_{ij} \frac{\hbar^2}{12(kT)^2} \left[ \frac{e_i e_j}{m_i} \delta(r_{ij}) - i \frac{1}{2kT} \left( \frac{e_i e_j}{r_{ij}} \right)^2 \right] \right\| \ll 1 \tag{62} \]
is fulfilled and the integrand may be approximated by
\[ e^{\varepsilon V} e \sum_{k=0}^{\infty} \frac{\hbar^k}{k!} \omega_k = e^{\varepsilon V}. \tag{63} \]

For \( r^2 < \lambda r_w \) the development (59) does not converge and we must look for another representation. For two particles approaching each other to such small distances the potential energy is dominated by their own interaction \( V \approx V_{ij} = e_i \cdot e_j / r_{ij} \). Under these circumstances their contribution \( w_{ij} \) to \( w \) may be factorized and is given by
\[ \frac{3w_{ij}}{\beta} - e^{\varepsilon V_{ij}} \left\{ \hbar \left[ \left( \frac{p}{M} \nabla_R + \frac{p}{\mu} \nabla_P \right) w_{ij} e^{-\varepsilon V_{ij}} \right] + \frac{\hbar^2}{2} \left[ \left( \frac{\Delta_R}{M} + \frac{\Delta}{\mu} \right) w_{ij} e^{-\varepsilon V_{ij}} \right] \right\} = 0 \tag{64} \]

where we have introduced relative \((r, p)\) and center of gravity \((R, P)\) coordinates and momenta. With the Ansatz
\[ w_{ij} = e^{\hbar} \omega(r) e^{\frac{e_i e_j}{r}}, \tag{65} \]

\( \omega(r) \) is defined by the equation
\[ \frac{\hbar^2}{2\mu} \Delta \omega + \frac{i\hbar}{\mu} p \nabla \omega - \frac{e_i e_j}{|r|} \omega = 0 \tag{66} \]
As is readily proven by substitution the solution of eq. (66) for small values of \( r \) can be represented by the development

\[
\omega = \sum_s \left( A_s |r|^s + \frac{B_s}{|r|^{s+1}} \right) \phi_s
\]

where \( \phi_s \) are the Legendre Polynomials. Due to the integration over the angles in the partition function the term \( s = 0 \) is dominant. The boundary condition of classical behaviour for \( r^2 > \lambda r_w \) determines \( A \approx 1 \) and \( B \approx 0 \) so that we finally have

\[
w_{ij} = e^{\frac{2i}{m} \rho \frac{\beta}{r}} e^{\frac{e_i e_j}{|r|}}
\]

In view of the results (53) and (68) we claim that the classical partition function

\[
Q_{fc} = \prod_{i=+,-} \left( \frac{2 \pi m_i k T}{\hbar^2} \right)^{3/2} \frac{1}{(N_f!)} \int e^{-\beta V} \text{d}r
\]

is applicable provided that the integration over the \( \mathbb{I}^7 \) -space is limited to interparticle-distances \( r^2 > r_w \lambda \).

Our claim is correct if the following two relations hold:

For pairs of oppositely charged particles

\[
\begin{align*}
\int_0^{c r_0} & \int_0^{\infty} e^{-\beta \left( \frac{p^2}{2\mu} - \frac{e^2}{|r|} \right)} \text{d}r \text{d}p \\
\int_0^{c r_0} & \int_0^{p_{\text{min}}} e^{-\beta \left( \frac{p^2}{2\mu} - \frac{e^2}{|r|} \right)} \text{d}p \text{d}r \\
\int_0^{c r_0} & \int_0^{\infty} e^{-\beta \left( \frac{p^2}{2\mu} - \frac{e^2}{|r|} \right)} \text{d}p \text{d}r \\
\int_0^{(\lambda r_w)^{1/2}} & \int_0^{\infty} e^{-\beta \left( \frac{p^2}{2\mu} - \frac{e^2}{|r|} \right)} \text{d}p \text{d}r
\end{align*}
\]

\[
= 1 - \kappa_0 \kappa 1
\]
For pairs of equally charged particles

\[
\int_0^{\infty} \frac{-\beta e^2}{|r|} \Omega e^{-\beta e^2/|r|} dr = 1 - \int_0^{(\lambda r_w)^{1/2}} \frac{c r_0}{(\lambda r_w)^{1/2}} e^{-\beta e^2/|r|} dr = 1 - \kappa_e \approx 1
\]

where according to eq. (68) \( \Omega \) is given by

\[
\Omega = \begin{cases} 
-\beta e^2/r & \text{for } r < (\lambda r_w)^{1/2} \\
1 & \text{for } r > (\lambda r_w)^{1/2}
\end{cases}
\]

and \( c \) is a numerical factor accounting for the uncertainty of the boundary of the pair approximation \( \mathcal{O}(c) = 1 \).

To evaluate eqs. (70) and (71) we employ the transformations

\[
y = \frac{r_w}{|r|}, \quad x = \frac{p}{\sqrt{2\pi} nKT}, \quad \epsilon = \frac{r_w}{c r_0}
\]

The limitation \( p > p_{\text{min}} \) in eq. (70) is due to the fact that the free particles can have only energy states above the limit given in eq. (92) and with the transformations (73) this limitation reads

\[
x^2 \geq y - \epsilon
\]
Using eqs. (73) and (74) in eqs. (70) and (71) we find

\[
\kappa_0 = \frac{4}{\sqrt{\pi}} \int_0^1 \frac{e^{-y} \left[ e^{-\frac{\lambda^2}{y^2}} \right] \frac{dy}{y}}{\varepsilon} \int_0^{\varepsilon} e^{y} \frac{dy}{y^4}
\]

and

\[
\kappa_e = \frac{4}{\sqrt{\pi}} \int_0^1 \frac{(e^{-y} - 1) \frac{dy}{y^4}}{\varepsilon} \int_0^{\varepsilon} e^{y} \frac{dy}{y^4}
\]

Evaluation of these integrals results in

\[
\kappa_0 = \frac{10^{-2}}{e^{3/2}} \left( \frac{\lambda}{r_w} \right)^{3/2} \frac{1}{N_D} \kappa_e \approx \kappa_0^2
\]

which shows that our claim is justified since the number \( N_D \) of particles in the Debye sphere is large.

Rigorously the classical approximation to the partition function justified above is subject to corrections for extremely high temperatures where \( \lambda \gg r_w \) holds. These corrections are due to additional contributions from the range \( r_w < r < \sqrt{r_w} \) and exchange degeneracy effects below \( \lambda \).
THE SAHA EQUATION

There are two reasons why the previous results cannot be directly applied to the formulation of the partition function of $N$ electrons and protons.

First the subdivision into bound and free particles is variable since we have ionization and recombination. Second due to quantum-mechanical effects and strong correlations the contribution from the range $E_b < E < E_f$ cannot be evaluated.

To overcome these difficulties we start from the following pair representation neglecting all interaction except within the bound state:

$$ Q = (\sigma_0 + \sigma_1 + \sigma_2)^N $$ \hspace{1cm} (78)

with

$$ \sigma_\mu = \int_{E^{(1)}_\mu}^{E^{(2)}_\mu} \frac{\mu}{e^\mu} g_\mu(e) e^{-e} \, de $$ \hspace{1cm} \mu = 0, 1, 2 \hspace{1cm} (79)

$$ g_0 = \sum_v R_v \delta(e - E_v) \frac{1}{e_v} $$ \hspace{1cm} $$ g_2 = \frac{4\pi(2m)^{3/2}}{\hbar^3 n_f^{1/2}} \hspace{1cm} (80)

$$ g_1 = g_0 \text{ for } E^{(1)}_1 < e < 0 $$ \hspace{1cm} $$ g_1 = g_2 \text{ for } 0 < e < E^{(2)}_1 $$

and

$$ E^{(1)}_0 = -R \hspace{1cm} E^{(2)}_0 = E^{(0)}_1 = -\frac{e^2}{r_0} \hspace{1cm} E^{(1)}_2 = E^{(2)}_2 = \infty $$ \hspace{1cm} (81)

Note that the factor $n_f = N_f / V$ in the denominator of $g_2$ accounts for the symmetry principle.
If we allow now for the interaction within the free group we know from diagram techniques and other methods that the effect in \( \tilde{\sigma}_\ell \) can be taken into account by using the new weight function \( g_\ell(\xi + E_D) \).

The correction in the integration limits is negligible.

Since principal obstacles (strong correlations and quantum-mechanical effects) prevent the evaluation of \( \sigma_1 \), we determine this weight function by interpolation between \( \sigma_0(\xi^{(j)}) \) and \( \tilde{\sigma}_\ell(\xi^{(j)}) \). The corresponding uncertainty is small since the interpolation interval is small and the weight function steady and monotonous. We find

\[
\begin{align*}
g_1(\xi) &= \frac{1}{2} \left( c_2 \left( \frac{\xi^2}{R_0} + E_D \right) - c_1 \left( \frac{\xi^2}{R_0} \right)^{3/2} \right) + \frac{c_2}{\xi^{3/2}} + \frac{c_1}{\xi^{1/2}} \\
&= \frac{1}{2} \left( c_2 \left( \frac{\xi^2}{R_0} + E_D \right) \right)^{1/2} + c_1 \left( \frac{\xi^2}{R_0} \right)^{-5/2}
\end{align*}
\]

with

\[
\begin{align*}
c_1 &= \frac{2}{3} R_0^{3/2} \\
c_2 &= \frac{4\pi(2n_f)}{h^3}
\end{align*}
\]

If we introduce eqs. (79)-(83) into (78) we have the partition function.

Applying the trinomial formula we arrive at

\[
Q = \sum_{\nu} \sum_{\xi} \binom{N}{\nu} \binom{\nu}{\mu} \sigma_0^{N-\nu} \sigma_1^{\nu-\mu} \sigma_2^\mu
\]

Each term of this sum gives the probability for the realization of a certain subdivision of our system into bound, quasi-free and free particles.
The most probable term corresponding to the Saha equation is found by minimization. This results in

\[
\frac{(v-u)}{N-v} = \frac{\sigma_1}{\sigma_0}, \quad \frac{\mu}{v-u} = \frac{\sigma_2}{\sigma_1}
\]

(85)

From this we obtain with \( \gamma = N_f \); \( N-\gamma = N_b \) the Saha equation.

\[
\frac{N_f^2}{N_b} = 2V \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \beta \frac{\varepsilon_f}{\varepsilon} - \beta \left( \frac{e^2}{D} - 0.4 \frac{e^2}{D} \right) \frac{\sum \varepsilon_n}{\varepsilon_n} e^{-\beta \varepsilon_n}
\]

(86)

Clearly the effect of the particle interaction on the Saha equation is reflected in two changes:

1) The influence on the single particle partition function \( \sigma_0 \).
2) The addiional terms in the exponent.

In the single particle partition function the energy eigenvalues may be represented by the eigenvalues of the hydrogen atom. The contribution to the partition function from the range between \( \varepsilon_h \) and \( \varepsilon_b \) is generally small and one can approximate it by an integral using the level density prescribed by the hydrogen atom \( \rho_c(\varepsilon) \).

It is customary to call the additional terms in the exponential factor the effective lowering of the ionization potential \( \Delta \chi \), in the Saha equation

\[
\Delta \chi = \frac{e^2}{D} + 0.4 \frac{e^2}{D}
\]

(87)

Remembering that the classical value \( \Delta \chi \) calculated with weak pair correlations neglecting free bound interaction is
\[ \xi \propto \frac{\alpha^2}{D} \]

we find a "correction term"

\[ \xi \propto \frac{1}{D} \frac{\varepsilon^2}{D} \]

This is obviously an order of magnitude larger than the corrections to \( e^2/D \) calculated from the cluster expansion.

There are two reasons for this difference: One of them is that in the range \( \varepsilon_b < \varepsilon < \varepsilon_f \) quantum-mechanical and strong correlation effects produce corrections much larger than those calculated from weak correlations. The other is caused by the new definition of the free-bound limit (see also ref. 32).

RESULTS

I. Of course, there is in principle a continuous transition between free and bound states. The introduction of a discontinuous boundary is therefore necessarily artificial and afflicted with an inherent uncertainty. With this in mind the evaluation of eq. (45) shows that the energy \( \varepsilon_b \) characterizing the "free-bound-limit" is roughly determined by

\[ \varepsilon_b \approx -\frac{e^2}{r_0} \]

II. The introduction of a discontinuous limit for "hydrogen-like behaviour" suffers from inherent uncertainties similar to those mentioned in the previous section. The definition of this limit underlying eq. (46) classifies all states as "non-hydrogen-like" for which the perturbation is of the same order of magnitude as the zero order hydrogen function. Since for large values of the principal quantum
number $\langle \mathbf{n} | \frac{\xi}{r} | \mathbf{n} + 1 \rangle \approx \langle \mathbf{n} | \frac{\xi}{r} | \mathbf{n} \rangle$ holds, eq. (46) defines our limit

$$\frac{1}{kT} \left( \frac{e^2}{r_0^2} \langle \mathbf{n} | \frac{\xi}{r} | \mathbf{n} \rangle \right)^2 = | \varepsilon_{n_h} - \varepsilon_{n_h + 1} | .$$

Due to the fluctuation of the microfield the eigenstates above this limit contribute to the continuous spectrum.

III. A classical approximation of the total partition function of a plasma is not possible. To the extent that the above defined "free" and "bound" states can be treated as independent particle groups the partition function may be composed of two factors. The factor accounting for the bound states is quantum-mechanical. The factor representing the free states can be described quasi-classically by the classical canonical partition function with the exclusion of interparticle distances $r^2 < \lambda r_w$.

IV. The ionization energy is defined as the energy required to bring an electron-ion pair from the lowest bound to the lowest free state. Utilizing the result for the free-bound limit and accounting for the weak pair correlation of the free particles the above definition gives for the lowering of the ionization energy

$$\Delta \epsilon = \frac{e^2}{r_0} + \frac{e^2}{D} .$$

The effective lowering of the ionization energy in the Saha equation is according to eq. (86) given by

$$\Delta \epsilon_{\text{Saha}} = 1, \frac{e^2}{D} = \Delta \epsilon + \Delta \epsilon_{\text{Saha}} .$$

Whereas the corrections to the Debye-Hückel term $\Delta \epsilon$ calcu-
lated from classical cluster theory and the naive free-bound definition are negligible below the critical density, the correction term derived here is of the same order of magnitude as the Debye term.

DISCUSSION

DIVERGENCE OF THE ATOMIC PARTITION FUNCTION. The divergence problem of the partition function of the hydrogen atom arises in the plasma due to the unjustified application of \( C_n \)-space statistics. Within this frame previous investigations\(^1\)\(^-\)\(^9\) avoid the difficulty by calculating limitations due to the influence of various surrounding effects.

In our \( F \)-space treatment, the divergence does not occur since it is found that the hydrogen atom is a possible model only below the limit given in eq. (92).

SHIFT AND BROADENING. As was already stated above, shift and broadening are of interest here only to the extent that they cause a depression of the series-limit and a change in the partition function. The series-limit derived in this paper (eq. 91) is different from the Inglis-Teller limit\(^1\)\(^0\), the ratio being \( (r_0/D)^{1/2} \). The reason is, that the static approach underlying the Inglis-Teller formula breaks down near \( \varepsilon_n \). It is understood that for \( \varepsilon_n > \varepsilon_b \) the series-limit is given by \( \varepsilon_b \). For low energy levels the Inglis-Teller formula is recovered.

Our investigation gives no energy change for the low bound states in contrast to the results in Ref. (12). It appears that the latter results are based on an incorrect perturbation theory, since a hydrogen atom in a low energy state does not polarize the plasma.
DIVERGENCE OF THE CLASSICAL PARTITION FUNCTION. The separation into free and bound states gives a lower energy limit for the free states. The evaluation of the quantum mechanical partition function with the energy limitation found above, shows that the classical canonical partition function without energy limitation and without the contributions from interparticle distances $\lambda^2 < \lambda r_w$ is a sound approximation. This exclusion of short range contributions removes the divergence of the classical partition function. It does not affect the numerical results of previous evaluations since those implicitly excluded short range contributions anyhow. This last result does not agree with strong deviations calculated elsewhere\(^{15}\) accounting for the energy limitation but neglecting all other quantum mechanical effects and making an inconsistent use of the Poisson-Boltzmann equation.

In another paper\(^ {14}\) it has been shown that the quantum mechanical partition function of a fully ionized plasma can be approximated by a classical canonical distribution with an effective short range interaction. This calculation is limited to extremely high temperatures ($\lambda > r_w$).

In the range $\xi_b < \xi < \xi_f$ the evaluation is very complicated due to quantum mechanical and strong correlation effects. Therefore approximations like our interpolation shown in Fig. 2 are inevitable.

LOWERING OF THE IONIZATION ENERGY. Using the direct definition of the ionization energy we have shown in eq. (92) that the lowering of the ionization energy is

$$\Delta X \approx \frac{e^2}{r_0} + \frac{e^2}{D}$$

(94)
Except for the uncertain numerical factor this formula agrees with the result derived from Unsöld's concept accounting at the same time for the effect of weak pair interactions.

The effective lowering of the ionization energy in Saha's equation as described by formula (93) is not identical with \( \Delta \chi \). Neither does it agree with the Debye term \( \Delta \chi \).

The difference between \( \Delta \chi \) and \( \Delta \chi_{\text{Saha}} \) may be elucidated in the following way. All free particle states are affected by free-bound and free-free interaction. In the lowest free state to which \( \Delta \chi \) refers the free-bound interaction dominates through the term \( e^2/r_0 \). With increasing energy however, the free-bound interaction becomes negligible in comparison to the Debye term of the free-free interaction. Since all free states contribute to the Saha equation it is evident that

\[
\Delta \chi = \frac{e^2}{D} < \Delta \chi_{\text{Saha}} < \Delta \chi \approx \frac{e^2}{r_0} + \frac{e^2}{D}
\]

holds.

This situation is demonstrated in the following figure (2), which shows the probability density of the pair representation. The light curve describes the case without interaction, whereas the heavy curve gives the probability density with free-free and free-bound interaction as approximated in this paper. The dotted line is based on the false assumption that the contribution of the free-bound interaction is independent of the free particle state; this assumption would produce \( \Delta \chi_{\text{Saha}} = \Delta \chi \).

The correction to the Debye term as calculated here is much stronger than the correction found from classical cluster expansions.
The reasons are the new free-bound definition accounting for the free-bound interaction, quantum-mechanical effects and strong correlations below $E = E_f$. Here it is quite obvious that a claim of accuracy of one per cent$^{23}$ cannot be substantiated.

Different values of the lowering of the ionization potential calculated with the use of different thermodynamic potentials are caused by errors in the analysis.

The plasma interaction also affects the Saha equation through the limitation of the single particle partition function. For temperatures low enough, so that the higher terms in the partition function do not contribute, this effect is of course negligible. As it becomes important with increasing temperatures the limitation is determined by $e^2/r_0$ and not by $e^2/D$ as suggested in Ref. (23).

The above formalism requires extension where the neutral-neutral interaction is important. This is the case for the interpretation of the surprising results found from experiments under extreme pressures.

Acknowledgement

Part of this work was carried out during our stay at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado. We would like to express our gratitude to the chairman and the members of JILA for their hospitality.

Editor's Comments:

A large part of the discussion at the conference concerned these results of Ecker and Kröll and, for details, reference should be made to the "Summary of Discussions."
REFERENCES

27. D.J. Blochinzew, Grundlagen der Quantenmechanik,
28. Y.N. Ryabinin, Gases at High Densities and Temperatures,
FIGURE CAPTIONS

Fig. 1  Schematic representation of the terminology and definitions used in the text.

Fig. 2  Weight function $g(E)$ used in the calculation of the partition function: Light curve - $g(E)$ as calculated for an isolated atom and a free electron-ion pair without interaction. Dotted curve - $g(E)$ as derived under the false assumption of a free-bound interaction independent of the free particle state. Heavy line - correct $g(E)$ curve.
Figure 1
II. STATISTICAL MECHANICS OF A PARTIALLY IONIZED PLASMA

by

J. L. JACKSON and L. S. KLEIN

DEPARTMENT OF PHYSICS
HOWARD UNIVERSITY

The following report describes some work in progress on the statistical mechanics of a partially ionized plasma. The object of this research is to attempt to incorporate a quantum mechanical treatment of the atomic states in a manner consistent with the usual Debye-Hückel approximation\(^1\) for fully ionized plasmas.

The immediate problem which is studied is that of calculating the equilibrium composition of a partially ionized plasma as a function of temperature and pressure on the basis of a fundamental statistical mechanical theory. It is felt that only on the basis of a fundamental theory can this conflict among the various theoretical discussions of the lowering of the ionization potential be examined critically. The particular form of statistical mechanical theory to be applied is the "distribution of potential method."\(^2\) This method appears to be singularly useful for the evaluation of the chemical potentials of the different constituents of a partially ionized plasma.

With the distribution of potential method, the chemical potential of a constituent species is expressed in terms of the probability distribution of its interaction potential. For the simple case of a fluid consisting of a single constituent with no internal degrees of freedom and a pairwise interparticle interaction potential, \(U(r)\), we can show that the chemical
potential can be written as:

$$\mu = kT \ln \frac{N \lambda^3}{V} - kT \ln \int d\phi e^{-\phi/kT} P(\phi),$$

(1)

where \( P(\phi) \) is the probability distribution function of the potential. The potential at a point is

$$\phi(r) = \sum_{i=1}^{N} U(r - \vec{r}_i).$$

(2)

As the fluid is homogeneous \( P(\phi) \) the probability distribution of the potential is independent of the point at which it is evaluated. In this form, the formula has been applied to a hard sphere gas; and, with the necessary extensions, to a fully ionized plasma. The problem of calculating the chemical potential, and hence, the free energy is, therefore, reduced to the problem of calculating the probability distribution function of the interaction energy, for which one often has available useful statistical methods. To apply this type of formula to the calculation of the equilibrium composition of a partially ionized plasma, it is necessary to obtain a suitable quantum mechanical generalization of Eq. 1. One can then write an expression for \( \mu_a \), the chemical potential of an atom, in terms of the statistics of the interaction between an atom and the plasma. A basic difficulty encountered in obtaining such a generalization is related to the fact that the Hamiltonian of the atom does not commute with the interaction between the atom and the plasma. One must, therefore, use quantum statistical perturbation procedures. The result of such procedures is that the leading term in the formula for \( \mu_a \), obtained by disentangling the non-commuting operators, is an analog of Eq. 1. However, one obtains quantum mechanical corrections, which can, under certain conditions, be shown to be small. Neglecting these small quantum mechanical corrections, the leading term in
the formula for chemical potential of the atom is:

\[
\mu_a = kT \left[ \ln \frac{N_a^\lambda}{\nu} - \ln \left\{ \int d\phi_1 d\phi_2 \sum_n \langle n | P(\phi_1 \phi_2) e^{-\delta[H_0 + e\phi_1 - e\phi_2]} | n \rangle \right\} \right]
\]

(3)

where the sum over \( n \) indicates a sum over the bound states of the atom and \( H_0 \) is the Hamiltonian of an unperturbed hydrogen atom. To evaluate this expression for \( \mu_a \) we must calculate \( P(\phi_1 \phi_2) \) the joint probability distribution of the potential at two points as a function of the distance between them. The two points are, of course, the locations of the electron and proton of the hydrogen atom. It may be ascertained that in the spirit of the Debye-Hückel description of a plasma, one has:\(^3\)

\[
P(\phi_1 \phi_2) = \frac{1}{2\pi kT(1 - \sigma^2)^{1/2}} \exp \left[ -\frac{\sigma^2 + \frac{2}{\sigma} - 2\sigma \phi_1 \phi_2}{2kT(1 - \sigma^2)} \right]
\]

(4)

with

\[
\sigma = \frac{1 - e^{-\kappa r}}{\kappa r}
\]

(5)

In the above, \( \kappa \) is the reciprocal Debye length and \( r \) is the distance between the two points at which one evaluates the potential. Using Eq. (4) in Eq. (3) and performing the indicated integration, one obtains an effective Hamiltonian for the atom, given by,

\[
H_{\text{eff}} = H_0 + \frac{e^2}{r} - \frac{e^2 e^{-\kappa r}}{r} - e^2 \kappa \cdot
\]

(6)

Although Eq. (4) is an unrealistic expression for \( P(\phi_1 \phi_2) \) when \( \phi_1 \) and \( \phi_2 \) are the potentials evaluated at points which are very close to each other, Eq. (6) is instructive in that it presents a consistent statistical mechanical approach in the spirit of Debye-Hückel Theory. Thus Eq. (6) enables one to critically examine other works that attempt an equivalent description.\(^4,5,6\)
In particular the Schrödinger equation which must be solved for the atomic energy levels is:

$$\left[ -\frac{\hbar^2}{2m} \psi^2 - \frac{e^2}{r} - e^2 \kappa \right] \psi = E \psi$$

so that the low lying excited states are essentially unshifted from the corresponding hydrogenic values. Thus, on the basis of a consistent Debye-Hückel approximation the constant shift, $e^2 \kappa$, obtained by G. Harris\textsuperscript{4} seems to be in error.

Within the framework of the above treatment the natural cut-off for the atomic partition function is then, the energy level $e^2 \kappa$ below the unperturbed energy zero for the hydrogen atom. In addition, the so-called lowering of the ionization potential, or the term which appears subtracted from the unperturbed hydrogen atom ionization potential in the Saha equation would be simply $e^2 \kappa$, coming from the Debye-Hückel free energy of the fully ionized component. As can be seen from the above treatment, there are no contributions to the free energy of the bound state component, aside from the shifted energy levels and small quantum mechanical corrections which occur due to the use of the effective Hamiltonian in Eq. (6).

It should be emphasized, that in the above treatment we have not specified the many-body wave functions of the partially ionized plasma. Instead, we have concentrated on deriving an effective Hamiltonian to be used with the single particle bound eigenstates. For this reason, no terms appear which would correspond to the leaking of an electron in a high energy atomic state through the potential barrier to the nearest neighbor ion. This is the effect proposed by Ecker and Kröll at this conference which leads them to the Unsöld cut-off. The feeling of the present authors is that this effect, if treated
by a quantitative localizability criterion which distinguishes the highly excited states from the free ion and electron states, would lead to a result in perturbation theory which gives corrections to the "lowering of the ionization potential" beyond those derived from Debye-Hückel theory. That the order of magnitude of these terms would correspond to those derived by Ecker and Kröll, is not at all obvious.
REFERENCES

1. P. Debye and E. Huckel, Phys. Z. 185 (1933)
2. J. L. Jackson and L. S. Klein, Phys. Fluids 7 228 (1964)
6. G. Harris, Phys. Rev. 133, 427 (1964)
III. EFFECTIVE DISSOCIATION AND IONIZATION ENERGIES IN PARTLY IONIZED AND DISSOCIATED GASES†

by

Adolf R. Hochstim
Institute for Defense Analyses
400 Army-Navy Drive
Arlington, Virginia 22202

For intermediate densities, the total Helmholtz free energy \( A \),

\( A = E - TS \) can be written as

\[
\frac{-A}{RT} = \frac{-A^0}{RT} + W - \frac{\rho}{\rho_0} \sum \sum i \sum j C_i C_j B_{ij}(T) - \frac{1}{2} \left( \frac{\rho}{\rho_0} \right)^2 \sum \sum \sum i \sum j \sum k C_i C_j C_k C_{ijk}(T) + \ldots ,
\]

where \( \sum \) means summation over neutral species only*; \( C_i = N_i/N_0 \), i.e.,

the number of particles of \( i \)th species per number of all particles in

a reference state; \( A^0 \) is the ideal** Helmholtz free energy given by

\[
\frac{-A^0}{RT} = \sum_i C_i \left[ + y(i) - \frac{E_0^O(i)}{RT} + 1 - \ln C_i - \ln \left( \frac{\rho}{\rho_0} \frac{T}{Z_0T_0} \right) \right] ,
\]

\[
P_0 = Z_0\rho_0RT_0, \quad y(i) = -\left( \frac{E_0^O(i)}{RT} \right) , \quad P_0 = 1 \text{ atm}, \quad T_0 = 273.16^\circ K ,
\]

(in the above notation, one must multiply all neutral-charge terms* by 2

in a double sum and by 3 in a triple sum).

†As in introduction, the first part of this paper is copied with slight changes from various parts of the author's paper presented at the 5th AGARD (NATO) Colloquium on "Theoretical Calculation of Thermodynamic Properties of Air," April 9-13, 1962 in Braunschweig, West Germany.

* E.g., for \( A \), \( A^+ \) and electrons:

\[
\sum_1 \sum_1 C_i C_j B_{ij} = C_{iA}^2 B_{A,A}^2 + 2C_{iA} C_{A,+} B_{A,+} + 2C_{iA} C_{A,e} B_{A,e} ,
\]

** The \( y(i) \) includes the effects of various interactions on the partition function which are not here considered. The \( y(i) \) is -3.66512 + 3/2 ln \( M_i \) + 5/2 ln \( T \) + ln \( Q_{i,n} \), where \( M_i \) is atomic, or molecular weight of \( i \)-th species, \( Q_{i,n} \) is the internal partition function.
$F^o$ is the ideal Gibbs free energy of the $i^{th}$ gaseous species; $W$ contains the contribution from interactions between the charged particles to the total Helmholtz free energy$^{2, 4, 12}$. $B_{ij}$ is the second virial coefficient accounting for the interactions between an $i^{th}$ and $j^{th}$ species for neutral-neutral and neutral-charged interactions only. The third virial coefficient $C_{ijk}$ accounts for the interactions between the $i^{th}$, $j^{th}$, and $k^{th}$ species. Here we again include only interactions of neutral-neutral-neutral or neutral-neutral-ion types, leaving in the contribution to $W$ all interactions between charged species.

Although the problem is, in general, very complex and no satisfactory theory and values for the interactions are available at the present time, the concentrations which multiply $B_{ij}$ and $C_{ijk}$ are, in many instances, so small that the contributions of such terms are negligible. Thus, for air at low temperatures, $C_{N_2^+ N_2, N_2} \approx 0$ because of the vanishing $N^+$; at very high temperatures, $C_{N_2 N_2^+ N_2, N_2} \approx 0$ because of vanishing $N_2$; etc. In principle, $B_{ij}$ can be obtained from a scattering experiment$^5$ or by using assumed potentials with constants deduced from an experiment (e.g., viscosity measurements). For the spherically symmetric interaction potential $V_{ij}(r)$ between the $i^{th}$ neutral and the $j^{th}$ neutral (or $j^{th}$ ionized) particle, the second virial coefficient is given by

\[
B_{ij} = -2\pi L \int_0^\infty \left( \exp \left[ \frac{V_{ij}(r)}{kT} - 1 \right] \right) r^2 \, dr, = B_{ij}, \quad (3)
\]
where \( L_0 \) is the Loschmidt number \( (L_0 = 2.6871 \times 10^{19} \text{ cm}^{-3}) \). For the Lennard-Jones (6-12) potential, tables are available in Ref. 5 for \( B^\ast(T^\ast) \), which is related by the following expression to \( B_{ij} \):

\[
B_{ij} = \frac{1}{V_0} (b_0)_{ij} B^\ast(T^\ast), \quad L_0 V_0 = N_A,
\]

where \( (b_0)_{ij} = \frac{2}{3} \pi N_A \sigma_{ij}^3 \), \( T^\ast = T/(\epsilon/k)_i \), \( \sigma_{ij} \) and \( (\epsilon/k)_i \) are listed in Ref. 5 and \( N_A \) is the Avogadro number, and

\[
\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}), \quad \epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}}.
\]

For charged particles, the contribution to the Helmholtz free energy can be written as

\[
\Delta(-A/RT) = \bar{W} = W_0 + W_M, \tag{5}
\]

where \( W_0 \) is the Debye-Hückel term which is exact to order \( \kappa^3 \), where \( \kappa \) is the reciprocal Debye length;

\[
W_0 = \frac{2}{3} \sqrt{\pi} \left( \frac{e^2}{kT} \right)^{3/2} \sqrt{L_0} \sqrt{\rho/\rho_0} \left( \sum C_i S_i \right)^{3/2} = \frac{1}{12\pi} \frac{\kappa^3}{\rho_0 L_0}, \tag{6}
\]

where \( \rho \) is the mass density, \( \rho_0 \) is the density at standard conditions,

\[
\kappa^2 = \frac{1}{d^2} = \frac{4\pi e^2}{kT} \left( \sum C_i S_i^2 \right) \frac{\rho}{\rho_0} L_0 = \frac{4\pi e^2 T}{kT} ; \quad N_i = C_i \frac{\rho}{\rho_0} L_0, \tag{7}
\]

where \( N_i \) is the particle density \( (\text{ cm}^{-3}) \), the dielectric constant for ionized gas \( D \) has been set equal to unity, and \( W_M \) is a term given by Mayer and Meeron.\(^2\)-\(^4\)
Let
\[ \Psi_{ij} = \frac{U^*_{ij}(r)}{kT}, \tag{8} \]
in which \( U^*_{ij}(r) \) is short range non-Coulombic type potential energy of interaction between charged species; then we can write\(^*\)
\[ W_M = -\frac{\rho}{\rho_0} \sum_i \sum_j C_i C_j \tilde{B}_{ij}, \tag{9} \]
where\(^3,4\)
\[ \tilde{B}_{ij} = 2\pi L_0 \int_0^\infty \left[ \exp \left[ -\Psi_{ij}(r) + k_{ij}(r) \right] + k_{ij}(r) - \frac{1}{2} k_{ij}^2(r) - 1 \right] r^2 dr, \tag{10} \]
and where (the same integral is given by Morita\(^6\) with \( U^* \) for the electron-proton interactions)
\[ k_{ij} = \frac{S_i S_j e^2}{kT} \frac{e^{-kr}}{r} \tag{11} \]
is the Debye-Hückel potential of average force divided by \( kT \), and \( S_i \) and \( S_j \) are charges on the \( i \)th and \( j \)th ion, respectively. Equation 1 through Meerow integral\(^4\) \( \tilde{B}_{ij} \) is exact through terms\(^**\) \( k^4 \) and \( k^4 \ln k \)

\(^*\) \( \tilde{B}_{ij} \neq 0 \) only for charged-charged species; e.g., for \( A, A^\prime \), and electrons \( \sum_i \sum_j C_i C_j \tilde{B}_{ij} = C_{A^+}^2 \tilde{B}_{A^+,A^+} + 2C_{A^+} C_e \tilde{B}_{e,A^+} + C_e^2 \tilde{B}_{e,e}. \)

\(^**\) i.e., up to and including terms with \( N_e^2 \) and \( N_e^2 \ln N_e. \) From Eq. 9 it follows that \( \tilde{B}_{ij} \) is exact through terms \( N_e^2 \) and \( \ln N_e. \)
and contains also incomplete parts of terms of higher order. In later derivations, we will find it useful to use the following integral:

\[ \tilde{B}_{ij}^{(2)} = - 2\pi L_0 \int_0^\infty \left\{ \exp \left[ \Psi_{ij}(r) + k_{ij}(r) \right] - k_{ij}(r) + 1 \right\} \times \]

\[ \times \exp \left[ -kr \right] r^2 dr. \]  

(12)

For the purpose of numerical evaluation of the integral \( \tilde{B}_{ij} \), we can integrate the last terms in \( \tilde{B}_{ij} \). Using the charge neutrality condition that \( \sum_i C_i S_i \sum_j C_j S_j = 0 \), we obtain

\[ W_M = -\frac{3}{8} W_0 - \frac{\rho}{\rho_0} \sum_i \sum_j C_i C_j \tilde{B}_{ij}^* \]  

(13)

\[ \Delta(-A/RT) = \frac{5}{8} W_0 - \frac{\rho}{\rho_0} \sum_i \sum_j C_i C_j \tilde{B}_{ij}^* = \frac{5}{96\pi} \frac{\kappa^3}{\rho_0 - L_0} - \frac{\rho}{\rho_0} \sum_i \sum_j C_i C_j \tilde{B}_{ij}^* \]  

(14)

where

\[ \tilde{B}_{ij}^* = - 2\pi L_0 \int_0^\infty \left\{ \exp \left[ \Psi_{ij}(r) + k_{ij}(r) \right] - 1 \right\} r^2 dr. \]  

(15)

The Debye-Hückel term \( W_0 \) is exact through term \( \kappa^3 \) and, although it now appears as \( \left[ 1 - (3/8) \right] W_0 \), the \( \tilde{B}_{ij}^* \) contain the term \( + 3/8 W_0 \). The reduced integrals \( \tilde{B}_{ij}^* \) can be evaluated numerically\(^7\) or by the methods of Poirier\(^6\) or Morita\(^8\). The short-range, non-Coulombic interaction potential can be taken as the short-range interaction potential between
hard spheres (see Eq. 33, etc.) with radius \( a_{ij} \), or by the method of Morita. 

We have for the compressibility\(^9\) of a partially ionized gas the expression

\[
Z = \frac{P}{\rho RT} = \left( \frac{\partial A/RT}{\partial \ln \rho} \right)_{T,C_i} = Z^* + \Delta Z = \sum C_i - \frac{1}{2} \left( \frac{\rho}{\rho_0} \right) W_0 - W_M
\]

\[
+ \frac{\rho}{\rho_0} K \frac{e^2}{kT} \sum_i \sum_j C_i C_j S_i S_j B_{ij}^{(2)} + \ldots + \frac{\rho}{\rho_0} \sum_i \sum_j \sum_k C_i C_j C_k C_{ijk} + \ldots ,
\]

or

\[
Z = \sum C_i - R_1 \sqrt{\frac{\rho}{\rho_0}} + R_2 \frac{\rho}{\rho_0} + R_3 \left( \frac{\rho}{\rho_0} \right)^{3/2} + R_4 \left( \frac{\rho}{\rho_0} \right)^2 + \ldots .
\]

Here

\[
R_1 = \frac{1}{3} \sqrt{\pi} \left( \frac{e^2}{kT} \right)^{3/2} \sqrt{\rho_0} \left( \sum C_i S_i^2 \right)^{3/2} = \frac{1}{2} W_0 / \sqrt{\rho/\rho_0}
\]

\[
R_2 = \sum_i \sum_j \tilde{C}_i C_j \tilde{B}_{ij} + \sum_i \sum_j \tilde{C}_i C_j \tilde{B}_{ij} ,
\]

\( \tilde{B}_{ij} \) and \( \tilde{B}_{ij}^{(2)} \) are still functions of \( \rho \), so that the expansion is only formal (see Eq. 46).
\[ R_3 = \sqrt{\pi} \left( \frac{e^2}{kT} \right)^{3/2} \sqrt{\lambda} \left( \sum c_i s_i^2 \right)^{1/2} \sum_i \sum_j \sum c_i c_j s_i s_j b_{ij}^{(2)}, \]

\[ R_4 = \sum_i \sum_j \sum_k c_i c_j c_k c_{ijk} + \ldots. \]

The chemical potential of the \( \ell \)th neutral species is

\[ \frac{\mu_\ell}{RT} = \left( \frac{\partial A}{\partial C_\ell} \right)_{T, \rho, C_j} = \frac{\mu_\ell^0}{RT} + 2 \frac{\rho}{\rho_0} \sum_i c_i b_{i\ell} + \frac{3}{2} \left( \frac{\rho}{\rho_0} \right)^2 \sum_i \sum_j c_i c_j c_{ijk} + \ldots, \]  

(18)

where \( \mu_\ell^0 \) is the chemical potential which is defined by the relation

\[ \frac{\mu_\ell^0}{RT} = -G(\ell) + \frac{E_0(\ell)}{RT} + \ln C_{\ell^+} + \ln \frac{1}{\rho_0} + \frac{T}{T_0}. \]  

(19)

The chemical potential of a \( k \)th ionized species is

\[ \frac{\mu_k}{RT} = \frac{\mu_k^0}{RT} - \frac{1}{2} s_k^2 \frac{e^2}{kT} + 2 \frac{\rho}{\rho_0} \left[ \sum_i c_i \bar{b}_{ik} + \sum_i \sum_j c_i b_{ik} \right] + \ldots + \]

\[ + \frac{\rho}{\rho_0} \frac{s_k^2}{\sum c_i s_i^2} \frac{\kappa}{2} \left( \frac{e^2}{kT} \right) \sum_i \sum_j c_i c_j s_i s_j b_{ij}^{(2)} + \ldots. \]  

(20)

Minimizing the total Helmholtz free energy at constant \( T \) and \( \rho \), and using Lagrange multipliers to account for the conservation of mass equation and for charge neutrality, we obtain a set of equilibrium
relations. Thus, for example, for the dissociation reaction \( \text{NO} = \text{N} + \text{O} \), we obtain

\[
\frac{c_{\text{N}}}{c_{\text{NO}}} = \frac{K_P}{c_{\text{NO}}} \exp\left[-\frac{D_{\text{eff}}}{RT}\right],
\]

(21)

or

\[
\frac{x_{\text{N}}}{x_{\text{NO}}} = \left(1 + \frac{\Delta Z}{Z^*}\right) \frac{K_P}{P_0} = \frac{K_P}{P_0 - \frac{\Delta Z}{Z_0} \frac{T}{T_0} \frac{\rho}{\rho_0}},
\]

(22)

where \( K_P^0 = \exp\left[Y(\text{N}) + Y(\text{O}) - Y(\text{NO})\right] \), \( Y = -(F^0 - E^0)/RT \), and

\( K_P = K_P^0 \exp\left[-D_{\text{eff}}/T\right] \); \( x_i \) are molar fractions, \( x_i Z^* = c_i \), \( Z^* = \sum c_i \), and

\( Z = Z^* + \Delta Z \); and we have defined the "effective dissociation energy" (in °K) as

\[
D_{\text{eff}}(\text{NO}) = D_0(\text{NO}) - 2Z^* \frac{\rho}{\rho_0} T \sum \dot{x}_i \dot{\beta}_i,\text{NO} - \frac{3}{2} T(Z^*)^2 \left(\frac{\rho}{\rho_0}\right)^2 \times
\]

\[
x \sum \sum \dot{x}_i \dot{x}_j \dot{\gamma}_i,\text{NO}^{+\cdots},
\]

(23)

\[
\beta_i,\text{NO} = B_i, N^+B_i, O^-B_i, \text{NO}
\]

\[
\gamma_{ijk} = C_{i,j}, N^+C_{i,j}, O^-C_{i,j}, \text{NO}
\]

(24)

The summation index \( i \) extends over all particles, including ionized atoms and molecules. As we see, \( D_{\text{eff}} \) is without contribution from
long-range Coulombic terms. To obtain concentration of species at high density, one needs to solve Eqs. 22 or 23 by an iteration procedure. For the dissociation of O₂ in air at $\rho/\rho_o=10$ at 3000°K and 6000°K, we obtain $D_{eff}-D_0(O_2)=45°K$ and 98°K, respectively. The stated results are still in the range of uncertainty of the dissociation energies.

For the singly ionizing reaction $A^0\rightarrow A^+ + e$, we obtain

$$\mu(A^+) + \mu(e) = \mu(A)$$

$$\frac{N_{A^+} + N_e}{N_A} = \frac{\rho}{\rho_0} \frac{C_{A^+} C_e}{C_A} = \frac{z_o L_o T_o}{T} \chi_p \exp \left[ - \frac{I_{eff}}{kT} \right], \quad (25)$$

where the "effective ionization energy" ($A$, $A^+$, and $e$ in a mixture of neutral and ionized atoms and molecules) which enters into Saha-type Eq. 25 is

$$I_{eff} = I_o(A) - e^2 k + 2kT \frac{\rho}{\rho_0} \left\{ \sum_i C_i \left[ B_{1i}, e + B_{1i}, A^+ \right] + \sum_i C_i \left[ B_{ii}, e + B_{ii}, A \right] - \sum_i C_i \left[ B_{ii}, A \right] \right\} +$$

$$+ \frac{\rho}{\rho_0} \sum_i \frac{kT}{C_i S_{ii} (kT)^2} \sum_j \sum_j C_i C_j S_{ij} S_{jj}^{(2)} \cdots -$$

$$- \frac{3}{2} kT \left( \frac{\rho}{\rho_0} \right)^2 \sum_i \sum_j C_i C_j S_{ij}, A^+ \cdots, \quad (26)$$
where I_o(A) is the standard ionization potential of A. The second term is the Debye-Hückel term, e^2/d. To obtain concentration of species from Saha-type Eq. 25, one usually uses an iterative procedure. A simple method for singly ionized gases was suggested by specifying electron concentration and the temperature, and solving for density.  

As a further illustration, rewriting Eq. 26 for weakly ionized pure argon (A, A^+, and e), we have (omitting third virial coefficients) for the change of ionization potential (in electron volts)

\[
I_{\text{eff}}(\text{ev}) - I_o(A) = \frac{T}{11605} \left\{ - \frac{e^2}{d} \frac{1}{kT} + 2 \frac{\rho}{\rho_o} \left[ C_{\text{A}^+} \left( \frac{\text{e}^+}{\text{e}}, \frac{\text{e}^+}{\text{e}}, \frac{-\text{e}}{\text{e}} \right) + C_{\text{e}} \left( \frac{-\text{e}}{\text{e}}, \frac{\text{e}^+}{\text{e}}, \frac{-\text{e}}{\text{e}} \right) \right] \right. 

+ C_{\text{A}} \left( \text{B}_A, \text{e}^+ \text{B}_A, \text{A}^+ \right) - \left( C_{\text{A}} \text{B}_A, \text{A}^+ \text{C}_{\text{A}^+} \text{B}_A, \text{A}^+, \text{A}^+ \text{C}_{\text{e}} \text{B}_A, \text{A} \right) + 

\left. \frac{\rho}{\rho_o} \left( \frac{e^2}{d} \left( \frac{C_{\text{A}^+} \text{b}^{(2)}_{\text{A}^+, \text{A}^+}}{C_{\text{e}} + C_{\text{A}^+}} \right) - \left( 2 C_{\text{A}^+} \text{C}_{\text{e}} \text{b}^{(2)}_{\text{A}^+, \text{e}} \right) + \left( \frac{C_{\text{e}} \text{b}^{(2)}_{\text{e}, \text{e}}}{C_{\text{A}^+}} \right) \right) \right\} . (27)

Using charge neutrality C_A = C_e and mass conservation C_A + C_A^+ = 1, the effective ionization potential (the last term in Eq. 27 vanishes for mixture with singly ionized species, see Eqs. 52 and 54) in electron volts is

\[
I_{\text{eff}}(\text{ev}) = I_o + \frac{T(\text{K})}{11605} \left\{ - \frac{e^2}{d} \frac{1}{kT} + 

+ C_{\text{e}} \frac{\rho}{\rho_o} \left[ 4 \frac{\text{B}_{\text{A}^+}, \text{e}^+ \frac{-\text{B}_{\text{A}^+}, \text{A}^+, \text{A}^+ \text{e}^+ \text{B}_A, \text{A}^-, \text{A}^+ \text{e}^+ \text{B}_A, \text{A}^-, \text{A}^+ \text{e}^+ \text{B}_A, \text{A} \right] \right. 

+ \left. \frac{2}{\rho_o} \left[ \frac{\text{B}_{\text{A}}, \text{e}^+ \text{B}_A, \text{A}^+, - \text{B}_{\text{A}}, \text{A} \right] \right\} . (23)
\]
The dimensionless $B_{ij}$ are given by Eq. 4

$$B_{ij} = \frac{(b_{ij})_{\infty}}{V_0} B_1 = 4.46 \times 10^{-5} \left(\frac{b_{ij}}{V_0}\right) B_1.$$ \hfill (29)

For neutral-neutral atoms and molecules\textsuperscript{1,5} for $1000 \leq T \leq 10,000^\circ K$,

$$10 \leq \left(\frac{b_{ij}}{V_0}\right) B_1 \leq 50 \text{ cm}^3 \text{ mole}^{-1}$$

so that for most atoms and molecules\textsuperscript{1,5}, one may take

$$4 \times 10^{-4} \leq B_{ij} \leq 2 \times 10^{-3}.$$ \hfill (30)

Thus, neutral-neutral contribution to the increase of ionization energy is at most

$$\Delta I_{ev} \leq 4(1-C_e) \times 10^{-7} \frac{\rho_o}{\rho} T,$$ \hfill (31)

e.g., at $T=5 \times 10^3 \text{ K}$ and $\rho/\rho_o=1$, it contributes at most $2 \times 10^{-3} \text{ ev}$, but at $\rho/\rho_o=10^2$ up to $0.2 \text{ ev}$.

Using potential for hard sphere, with diameter $a_{ij}$, for the short range potential, i.e.,

$$\psi_{ij}(r) = \infty \quad \text{for } r < a_{ij},$$ \hfill (32)
\[ \psi_{ij}(r) = 0 \quad \text{for } r \geq a_{ij}, \quad (33) \]

we obtain

\[
\begin{align*}
\frac{B_{ij}}{-2\pi L_0} &= -\frac{a_{ij}^3}{3} \int_{a_{ij}}^{\infty} \left( e^{-k_{ij}^2 + k_{ij}^2 - \frac{1}{2} k_{ij}^2 - 1} \right) r^2 dr + Qd^3 \\
&= -\frac{a_{ij}^3}{3} \int_{a_{ij}}^{\infty} \left[ -\frac{1}{3!} k_{ij}^3 + \frac{1}{4!} k_{ij}^4 + \cdots \right] r^2 dr + Qd^3, \quad (34) \\
Q &= \lambda_{ij} \left[ 1 + (1 + \beta_{ij}) e^{-\beta_{ij}} \right] - \frac{1}{4} \lambda_{ij}^2 \left( 1 - e^{-2\beta_{ij}} \right), \quad (34a)
\end{align*}
\]

where

\[
\begin{align*}
k_{ij} &= \frac{S_{ij} e^2 / d}{kT} e^{-x} = \frac{e^{-x}}{x} = \lambda_{ij} x; \quad x = r/d = rk \\
\lambda_{ij} &= \frac{S_{ij} e^2 / d}{kT}; \quad \beta_{ij} = a_{ij}/d = a_{ij} k \\
&= -\frac{1}{3} + \beta_{ij}^3 \int_{\beta_{ij}}^{\infty} \left[ -\frac{1}{6} \lambda_{ij} e^{-3x} + \frac{1}{24} \lambda_{ij} e^{-4x} - \cdots \right] x^2 dx + Q\beta_{ij}^{-3} \\
&= -\frac{1}{3} + a_{ij}^2 \int_{1}^{\infty} \left[ -\frac{1}{6} \lambda_{ij} e^{-3\beta_{ij} t} + \frac{1}{24} \lambda_{ij} e^{-4\beta_{ij} t} - \cdots \right] dt + Q\beta_{ij}^{-3},
\end{align*}
\]
where \( x = \beta t \) and where

\[
\alpha_{ij} = \frac{S_i S_j e^{2/a_{ij}}}{kT}.
\] (37)

Introducing generalized exponential integral\(^{15}\)

\[
E_n(Z) = \int_1^\infty \frac{e^{-Zt}}{t^n} \, dt,
\] (38)

\[
\frac{B_{ij}}{-2\pi L_o a_{ij}^3} = -\frac{1}{3} + \alpha_{ij}^2 \sum_{n=1}^\infty \frac{\alpha_{ij}^n (-1)^n}{(n+2)!} E_n[(n+2)\beta_{ij}] + Q_{ij}^3.
\] (39)

Since the above integral contains higher order terms which the derivation justifies, we will proceed (following Meeran\(^4\)) to evaluate \( B_{ij} \), keeping only terms containing \( \beta_{ij}^0 \) and \( \ln \beta_{ij} \) (i.e., only terms containing \( N_{e}^0 \) and \( \ln N_e \)).

Thus,

\[
E_1(Z) = -\gamma - \ln Z + \cdots,
\] \( \gamma = 0.577216 \) (40)

and using recurrence relation

\[
E_{n+1}(Z) = \frac{1}{n} \left[ e^{-Z} Z E_n(Z) \right]
\] (41)
\[ E_2(Z) = 1, \quad E_3(Z) = \frac{1}{2}, \quad E_4(Z) = \frac{1}{3}, \]

\[ E_5(Z) = \frac{1}{4}, \ldots, E_n(Z) = \frac{1}{n-1}, \quad (42) \]

and using expansion of \( Q \) in Eq. 34 (to order \( \beta_{ij} \)),

\[ \frac{E_{ij}}{2\pi L_0 a_{ij}^3} = \frac{1}{3} - \frac{a_{ij}^3}{6} \gamma + \ln^3 + \ln \beta_{ij} - \sum_{n=2}^{\infty} \frac{a_{ij}^{n+2}(-1)^n}{(n+2)!} \frac{1}{n-1} - 2a_{ij}^2 \beta_{ij}^2 + \frac{1}{2}a_{ij}^3. \quad (43) \]

The infinite sum can be evaluated by the method employed by Meeran.\(^4,16\)

Since

\[ \frac{1}{n-1} = \int_0^1 x^{n-2} dx = \int_0^1 x^{n+2} \frac{dx}{x^4} \quad (44) \]

and since

\[ e^{-\alpha_{ij} x} = 1 - \alpha_{ij} x + \frac{\alpha_{ij}^2 x^2}{2} - \frac{\alpha_{ij}^3 x^3}{6} + \sum_{n=2}^{\infty} \frac{(\alpha_{ij})^{n+2}(-1)^n}{(n+2)!} x^{n+2}, \]
\[ \sum_{n=2}^{\infty} \frac{\alpha_{ij}^{n+2} (-1)^{n}}{(n+2)!} \frac{1}{n-1} = \int_{0}^{1} \sum_{n=2}^{\infty} \left[ \alpha_{ij}^{n+2} (-1)^{n} \frac{1}{x^{n+2}} \right] dx \]

\[ \int_{0}^{1} \left[ e^{-\alpha_{ij} x} \left( -1 + \alpha_{ij} x - \frac{\alpha_{ij}^{2} x^2}{2} + \frac{\alpha_{ij}^{3} x^3}{6} \right) \right] \frac{dx}{x^4} = \text{I}(\alpha_{ij}). \quad (45) \]

Thus, finally

\[ \frac{\bar{E}_{ij}}{2\pi L_{o} a_{ij}^{3}} = \frac{1}{3} - \frac{\alpha_{ij}^{3}}{6} \left( \gamma + \ln 3 + \ln \beta_{ij} \right) - 2\alpha_{ij} \left( \frac{d}{a_{ij}} \right)^2 + \frac{1}{2} \alpha_{ij}^{2} - \text{I}(\alpha_{ij}) \], \quad (46) \]

where the last integral \( \text{I}(\alpha_{ij}) \) can be simply evaluated by numerical integration (see Table I).

The contribution to the Helmholtz free energy from charge-charge interactions is (see Eqs. 1, 5, and 9)

\[ W = \omega_{o} - 2\pi L_{o} \rho_{o} \sum_{i} \sum_{j} C_{ij} \left( \frac{a_{ij}^{3}}{3} - \frac{1}{6} \left( \frac{S_{ij} e^2}{kT} \right)^{3} \left( \gamma + \ln 3 + \ln a_{ij} \right) \right) - \frac{1}{2} \left( \frac{S_{ij} e^2}{kT} \right)^{2} a_{ij}^{2} - \frac{3}{2} \alpha_{ij}^{3} [\text{I}(\alpha_{ij})] \], \quad (47) \]
TABLE I

THE INTEGRAL $I(\alpha_{ij})$

<table>
<thead>
<tr>
<th>$\alpha_{ij}$</th>
<th>$I(\alpha_{ij})$</th>
<th>$\alpha_{ij}$</th>
<th>$I(\alpha_{ij})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>219.7</td>
<td>-0.2</td>
<td>6.80x10^{-6}</td>
</tr>
<tr>
<td>9</td>
<td>150.7</td>
<td>-0.4</td>
<td>0.00111</td>
</tr>
<tr>
<td>8</td>
<td>98.59</td>
<td>-0.6</td>
<td>0.00574</td>
</tr>
<tr>
<td>7</td>
<td>60.77</td>
<td>-0.8</td>
<td>0.01856</td>
</tr>
<tr>
<td>6</td>
<td>34.62</td>
<td>-0.9</td>
<td>0.03007</td>
</tr>
<tr>
<td>4</td>
<td>7.719</td>
<td>-1</td>
<td>0.04635</td>
</tr>
<tr>
<td>2</td>
<td>0.5579</td>
<td>-2</td>
<td>0.8375</td>
</tr>
<tr>
<td>1</td>
<td>0.03792</td>
<td>-4</td>
<td>18.15</td>
</tr>
<tr>
<td>0.9</td>
<td>0.02510</td>
<td>-5</td>
<td>53.62</td>
</tr>
<tr>
<td>0.8</td>
<td>0.01581</td>
<td>-6</td>
<td>139.2</td>
</tr>
<tr>
<td>0.6</td>
<td>0.005096</td>
<td>-7</td>
<td>335.8</td>
</tr>
<tr>
<td>0.4</td>
<td>0.001026</td>
<td>-8</td>
<td>780.0</td>
</tr>
<tr>
<td>0.2</td>
<td>6.54x10^{-5}</td>
<td>-9</td>
<td>1785.9</td>
</tr>
<tr>
<td>0.0</td>
<td>0.00000</td>
<td>-10</td>
<td>4091.7</td>
</tr>
</tbody>
</table>

\[
\alpha_{ij} \approx \frac{e^2}{kT} \approx \frac{16.6}{a_{ij}^o} \left( \frac{10^4}{T} \right) \Rightarrow \alpha_{ij} = a_{ij}^o \times 10^{-8} \text{ cm}
\]
or expanding in powers of \( \lambda, \lambda = (e^2 \kappa)/kT \), the Helmholtz free energy from charge-charge interactions only is (for a multi-component mixture)

\[
\frac{A_c}{kT} = \sum_i N_i S_i \left[ -\frac{1}{3} \lambda + \frac{1}{2} \lambda^2 \sum_j N_j N_{ij} \varphi_{ij} \right],
\]

where

\[
\lambda^2 = 4n \left( \frac{e^2}{kT} \right)^3 \sum N_i S_i^2,
\]

\[
\varphi_{ij} = \left( \frac{kT a_{ij}}{e^2} \right)^3 \left[ \frac{1}{3} - I(\alpha_{ij}) \right] + \frac{1}{2} S_i S_j \frac{kT a_{ij}}{e^2} - \frac{1}{6} S_i S_j S_j \left( \gamma + \ln 3 + \ln a_{ij} \right),
\]

and where the \( \frac{1}{3} \lambda \) term is the Debye-Hückel term. For a single cutoff radius \( a_{ij} = a \) and only singly ionized atoms,

\[
\frac{A_c}{N_e kT} = -\frac{2}{3} \lambda + \lambda^2 \left[ \frac{1}{3} \left( \frac{kT a}{e^2} \right)^3 + \frac{1}{2} \left( \frac{kT a}{e^2} \right)^2 - \left( \frac{kT a}{e^2} \right)^3 \right] \int_0^1 \left( \cosh \alpha x - \frac{1}{2} \alpha^2 x^2 - 1 \right) \frac{dx}{x^4},
\]
and if

\[ \alpha = \frac{e^2/a}{kT} < 1, \quad (50a) \]

\[ \frac{A_c}{N_e kT} \approx -\frac{2}{3} \lambda + \lambda^2 \left[ \frac{1}{3} \left( \frac{kT a}{e^2} \right)^3 + \frac{1}{2} \frac{kT a}{e^2} - \frac{1}{24} \frac{e^2}{kT a} \right]. \quad (51) \]

Equation 50 was obtained by Meeran,\textsuperscript{4,16} Eq. 51 by Jackson and Klein\textsuperscript{23} (with terms from Haga\textsuperscript{17}). If we use Eq. 50a, \( A_c \) for a mixture of \( S_+ \) and \( S_- \) times ionized positive and negative pair of ions reduces from Eq. 48 to that obtained by Jackson-Klein-Haga. Others\textsuperscript{6,17-22} obtained similar results for singly ionized plasmas, differing often in variously omitted terms of order \( \lambda^2 \). Following Meeran,\textsuperscript{4,16} the generalized Eqs. 46 and 48 are exact expressions up to and including order \( \lambda^2 \).

The last terms in Eqs. 20 and 27 can be evaluated by either expanding \( b_{ij}^q \) from Eq. 12 and integrating to terms containing \( \kappa^0 \) and \( \ln \kappa \), or simpler, by differentiation of Eq. 46 with respect to \( C_k \), i.e.,

\[ \left( \frac{\partial B_{ij}}{\partial C_k} \right)_{T, \rho, C_j} = -\frac{\pi L_o}{6} \frac{e^2}{(kT)^3} \sum C_i S_i^3 S_j^3 S_k^2 + \frac{4\pi L_o S_i S_j}{\kappa^2} \frac{e^2}{\sum C_i S_i^2 (kT)^2} \quad (52) \]

and the contribution of this term to the chemical potential of \( k \)th
ionic species is (last term in Eq. 20)

$$\frac{\Delta \mu_k}{RT} \text{(from } B^{(2)}) = -\frac{\pi}{6} \left( \frac{e^2}{kT} \right)^3 \sum_{i} \sum_{j} S_i^2 S_j^2 + \sum_{i} \sum_{j} N_i C_i S_i^3 S_j^3 +$$

$$+ \frac{4\pi S_k^2}{\kappa^2 \sum_{i} C_i S_i^2} \left( \frac{e^2}{kT} \right) \sum_{i} \sum_{j} N_i C_j S_i S_j,$$  \hspace{1cm} (53)

and to the ionization energy in Saha equation is (last term in Eq. 27)

$$\frac{\Delta I}{RT} \text{(from } B^{(2)}) = -\frac{\pi}{3} \left( \frac{e^2}{kT} \right)^3 \sum_{i} \sum_{j} \frac{1}{C_i S_i^2} N_i C_j S_i S_j^3 +$$

$$+ \frac{8\pi}{\kappa^2 \sum_{i} C_i S_i^2} \frac{e^2}{kT} \sum_{i} \sum_{j} N_i C_j S_i S_j.$$ \hspace{1cm} (54)

For singly ionized plasma,

$$\sum_{i} \sum_{j} N_i N_j S_i^3 S_j^3 = \left( \sum_i N_i S_i^3 \right)^2 = \left( \sum_i S_i \right)^2 = 0$$ \hspace{1cm} (55)

because of charge neutrality, and thus Eq. 54 does not contribute to the effective ionization energy of a gas with only singly ionized atoms.
SUMMARY

The contribution to the "effective ionization energy" of singly ionized atoms (mixture of A, A⁺, and e) in a Saha equation is (from Eqs. 28, 46, and 55)

\[ I_{\text{eff}}(\text{ev}) = I_0 - L_1 \sqrt{N_e} - L_2 N_e - L_3 N_e \ln N_e + L_4 (\rho/\rho_0) + \cdots, \]  

where

\[ L_1 = \frac{T(0 \text{ K})}{11605} \cdot \frac{2 \sqrt{2\pi e^3}}{(kT)^{3/2}} \]  

(Debye-Hückel term),

\[ L_2 = \frac{T}{11605} \cdot 2\pi \left( \frac{e^2}{kT} \right)^3 \ln \frac{a_{+,e}^2 + a_{+,e}^e}{a_{+,e}^e} + 4a_{+,e}^3 \left[ I(a_{+,e}) - \frac{1}{3} \right] + 2a_{+,e}^3 \left[ I(a_{+,e}) - \frac{1}{3} \right] - 2B_{A,e} - B_{A,e}^2 - B_{A,e}^A - \left( \frac{e^2}{kT} \right)^2 \left( 2a_{+,e}^2 + a_{+,e}^2 + a_{+,e}^2 \right) \]  

(58)

\[ L_3 = 0 \]  

(not so for multiply ionized atoms, see Eqs. 26, 46, (59) and 54)

and

\[ L_4 = 2 \left( B_{A,e} + B_{A,e} + B_{A,e} + B_{A,e} \right) \cdot \frac{T}{11605}. \]  

(60)
If a mixture of doubly, etc., ionized atoms are present, the general Eq. 26 with $b^{(2)}_{ij}$ term given by Eq. 54 gives $I_{\text{eff}}$

As an illustration, we take moderately-dense weakly-ionized gas having $\rho/\rho_0=100$, $T=10,000^\circ$ K, and $N_e=10^{18}$ cm$^{-3}$ and obtain the following order of magnitude estimates:

- From Debye-Hückel term: $\Delta I \approx -0.3$ ev
- From $L_2$ term ($a=1.66\text{Å}$): $\Delta I \approx -0.2$ ev
- From $L_2$ term ($a=4\text{Å}$): $\Delta I \approx -0.03$ ev
- From $L_2$ term ($a=16.5\text{Å}$): $\Delta I \approx +10^{-4}$ ev
- From neutral-neutral: $\Delta I \approx \pm 0.4$ ev
- From charge-neutral: $\Delta I \approx \pm 0.4$ ev

We see that terms of higher order than Debye from the charge-charge interactions contribute significantly to an "effective ionization energy" and that these depend strongly on the assumed value of the cutoff $a$. In principle, this can be corrected by using more accurate interaction potential $U^*$ (see Eq. 8). The contribution from neutral-neutral is more easily computed and this can be extended to ion-neutral interactions. Electron-neutral interactions can be computed by quantum mechanics from scattering phase shifts and their relation to the virial coefficient.$^5$

The term "effective ionization energy" originated as a mathematical convenience and cannot be a priori connected with the physical interpretation of the ionization energy. Thus what one obtains by minimization of free energy (see Eq. 25) is

$$\frac{N_{e+N^+_i}}{N_n} = f(T,\rho) \frac{2Q_i}{Q_n} e^{-\frac{(\text{I}_0)}{kT} e^{-\Delta}, \quad \Delta = \Delta(T,N_e)}.$$  \hspace{1cm} (61)
This is what one interprets as a Saha equation with an "effective ionization energy" given by

$$I_{\text{eff}} = I_0 - kT\Delta,$$

(62)

because one is forcing the transcendental equation for $N_e$ to look like a Saha equation (with $\Delta=0$). We could easily have associated $f(T,\rho)e^{-\Delta}$ or $Q_e e^{\Delta}$, etc.

We have minimized Helmholtz free energy and obtained Debye and higher order corrections (i.e., in $\Delta$) in a modified Saha-type equation. The question remains, "What is the physical interpretation of the concentrations of electrons in Eq. 61?" As pointed out by Ecker and discussed in the Boulder meeting, these may be free electrons or may also include some semi-bound electrons. It is not clear at all that these computed electrons correspond to the ones which produce the microwave attenuation (electric conductivity) or thermal conduction, or are deduced from spectroscopic or probes methods. The question is fundamental and still remains unsolved today.
REFERENCES


7. Lowain et al., Bull. Am. Math. Soc., 48, 739 (1942); corrigenda, ibid, 49, 939 (1943)


15. Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables, NBS Applied Mathematics Series No. 55, Department of Commerce, Washington, D. C. (June 1964)


III. ON THE EXISTENCE OF NON-PHYSICAL SOLUTIONS TO A SAHA-TYPE EQUATION IN THE PRESENCE OF LONG-RANGE INTERACTIONS

Adolf R. Hochstim
Institute for Defense Analyses
Arlington, Virginia

It is generally assumed that a Saha-type equation\(^1\)–\(^3\)

\[
\frac{C_e^2}{1-C_e} = 1.797 \times 10^{-4} \frac{Q(+) T \sqrt{T}}{Q(0) \rho/\rho_0} e^{-I_{\text{eff}}/kT},
\]

where \(N_e = C_e L_0 \rho/\rho_o\) and \(L_0 = 2.687 \times 10^{19}\) cm\(^3\), yields one value of electron concentration \(N_e\) for a given temperature \(T\) and density \(\rho\). Actually, there may be more solutions, of which only one is physically meaningful (see Fig. 1). There is a danger of obtaining the wrong solution in the commonly used iterative method at specified \(\rho\) and \(T\). A simpler method of solution is to specify \(T\) and \(N_e\) and to solve directly for the density\(^2\) with a condition \(N_e < N'_e\), where \(N'_e\) will be given later (Eq. 10). Thus solving Eq. 1 for \(\rho/\rho_0\), we obtain (using the Debye-Hückel correction only) for singly ionized species

\[
\frac{N_e^2}{N_0^0 - N_e} = \left(\frac{2\pi m_e kT}{\hbar^2}\right)^{3/2} \frac{2Q(+) e}{Q(0)} e^{-I_{\text{eff}}/kT},
\]

\[
\frac{\rho}{\rho_0} = \frac{N_e}{L_0} \left[\frac{1 + G N_e e^{-\lambda_0 \sqrt{N_e}}}{1 + G N_e e^{-\lambda_0 \sqrt{N_e}}}ight], \quad (3)
\]
where

\[ \lambda = \lambda_0 \sqrt{N_e} = \frac{e^2}{d} \frac{1}{kT}, \quad N_n^0 = \frac{\rho}{\rho_0}, L_0, \]

\[ G = \frac{Q(0) \exp(I_0/kT)}{1.797 \times 10^{-4} L_0 Q(+) T \sqrt{T}}, \]  \( (4) \)

and \( I_{\text{eff}} \) is the 'effective ionization energy', for example,

\[ I_{\text{eff}} = I_0 - \frac{e^2}{d}. \]  \( (5) \)

The reason for more than one solution is as follows. The equilibrium concentrations result from the minimization of total free energy, subject to charge and mass conservation. Mathematically, this is done by forming function \( \psi \), e.g., for two species,

\[ \psi = A + \lambda_1 (C_e^{-C_i}) + \lambda_2 (C_i + C_n - 1), \]  \( (6) \)

where \( C_e, C_i, \) and \( C_n \) are concentrations of electrons, ions, or neutrals, respectively; \( A \) is the free energy; and \( \lambda_1 \) and \( \lambda_2 \) are Lagrange multipliers. Then one sets

\[ \left( \frac{\partial \psi}{\partial C_e} \right)_{T, \rho, C_i, C_n} = \left( \frac{\partial \psi}{\partial C_i} \right)_{T, \rho, C_e, C_n} = \left( \frac{\partial \psi}{\partial C_n} \right)_{T, \rho, C_i, C_e} = 0. \]  \( (7) \)

Equation 7 yields the Saha equation and guarantees extremum of free energy. Therefore the Saha equation gives the necessary, but not sufficient, condition for the minimum. One can show that in the
absence of long distance interactions (Coulomb, virial), the additional requirement for the free energy to be minimum is that the concentrations be positive. If one includes the Debye-Hückel term in the free energy, one obtains the Saha-type equation (Eq. 1) with 
$I_{\text{eff}} = I_e - e^2/d$. Then, one must determine if the free energy was indeed minimized. It is found that the non-physical solution is the maximum (or stationary) value of the free energy.

Example: For a one element mixture of $x$, $x^+$, and electrons and with Debye-Hückel correction only to the free energy (see Eq. 5), one obtains as a condition for the minimum of free energy

$$\left( \frac{\partial^2 A / RT}{\partial C_e^2} \right)_{T, \rho} = \frac{2}{C_e} + \frac{1}{1-C_e} - \frac{1}{2C_e} \lambda > 0,$$  \hspace{1cm} (8)$$

where $\lambda = (e^2/d)/kT$ or

$$\lambda < 4 + \frac{2C_e}{1-C_e}; \hspace{1cm} 0 \leq C_e < 1.$$  \hspace{1cm} (9)$$

Since the Debye theory is valid only under the more restricted condition of $\lambda < 1$, we see that for singly ionized species the only additional requirement for a unique solution (guaranteeing minimum of free energy) is

$$\lambda = \frac{e^2/d}{kT} < 1.$$  \hspace{1cm} (10)$$

For an ideal gas ($\lambda = 0$), we see from Eq. 8 that the usual Saha equation corresponds to the minimum free energy since $C_e > 0$, $C_\rho = 1 - C_e > 0$, and the
positive value of concentrations are sufficient guarantees for the minimum. Differentiating Eqs. 1 and 3, we get

$$\left( \frac{\partial \ln n}{\partial \ln C_e} \right)_T = \frac{1}{2} \left[ \lambda - \frac{4 + 2C_e}{1 - C_e} \right] = -\frac{2C_e}{RT} \frac{\partial^2 A}{\partial C_e^2} \left( T, \rho \right)$$

(11)

or

$$\left( \frac{\partial \ln \rho}{\partial \ln N_e} \right)_T = 1 + \frac{N_e G e^{-\lambda}}{1 + N_e G e^{-\lambda}} \left( 1 - \frac{1}{2} \lambda \right).$$

(12)

The last derivatives are zero for

$$\lambda = 4 + \frac{2C_e}{1 - C_e} = 4 + \frac{2N_e}{N_o - N_e}.$$ 

The only physically-meaningful solution for an equilibrium is a unique solution with free energy being minimum, which corresponds to $\lambda < 1$. For $1 < \lambda < 4 + (2C_e/1 - C_e)$, the free energy is minimum but the Debye theory is not valid. For $\lambda = 4 + (2C_e/1 - C_e)$, the free energy has stationary value, corresponding to minimum or maximum in the plot of $\ln \rho$ versus $\ln N_e$. For $\lambda > 4 + (2C_e/1 - C_e)$, the free energy is maximum. The last two conditions have no physical significance.

In general, when one has a multicomponent mixture with variously ionized and dissociated species, with Coulomb and other interactions,
it is not possible to give a simple relation* for guaranteeing equilibrium solution based on the requirement that the free energy has an absolute minimum.

*There are no simple conditions for the minimum — and we need, in addition, the absolute (lowest) minimum \( \frac{g}{2} \) of a function with many variables and with subsidiary conditions.
REFERENCES


3. A. R. Hochstim, "Effective Dissociation and Ionization Energies in Partially Ionized and Dissociated Gases" (See elsewhere in this report.)

Density Versus Electron Concentration Based on $I_{\text{eff}} = I_0 \cdot e^{-2/d}$
IV. REVIEW OF CURRENT KNOWLEDGE OF EQUILIBRIUM PLASMA
STATISTICAL MECHANICS

by

Hugh DeWitt
University of California
Lawrence Radiation Laboratory
Livermore, California

This talk will deal with systematic and essentially rigorous
calculations of the thermodynamic properties of plasmas from statistical
mechanics. I use the word rigorous in the sense that one can obtain
results for the first few terms in expansions, and these results are correct
in some extreme temperature and density limits. Hopefully a knowledge of
the exact form of say the Helmholtz free energy of a high temperature
and low density plasma will be of help in giving information about the
intermediate temperature and density plasmas that are the concern of this
meeting.

\[
\begin{align*}
Z_N e^e + Z_N i^i &= 0 \\
V, \beta &= 1/kT \\
U_{\alpha\beta}(r) &= \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha\beta}} \\
\rho_e &= N_e/V, \quad \rho_i = N_i/V
\end{align*}
\]

The statistical mechanical problem
is formulated as follows: In a large
volume \( V \) there are \( N_e \) electrons and
\( N_i \) ions at a temperature \( T \). Electrical
neutrality is assumed, \( Z_N e^e + Z_N i^i = 0 \),
and only Coulomb interactions will be
discussed. Naturally in real plasmas
there may be neutral atoms and ions
with bound electrons which will also have
van der Waals interactions at short range.
For the moment we deal with point charges, say fully ionized hydrogen. We wish to calculate the canonical partition function (actually the grand partition function is used, but I will leave out mathematical procedures that are not too relevant);

\[ Z(\beta, \rho) = \text{Tr} e^{-\beta (H_0 + H_1)} = e^{-\beta F} \]

\[ F = E - TS \]

where

\[ H = H_0 + H_1 = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} + \sum_{\alpha < \beta} \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha \beta}} \]

\[ F = F_0 + F_I \]

Let me emphasize here something which everybody knows. For point charges, electrons and protons, the classical partition function diverges, and the quantum treatment is essential even for fully ionized plasmas in order that the partition function exist. Even when \( T \) is so large that no bound states exist the uncertainty principle is required to keep opposite changes from coalescing together.

A brief discussion of lengths and dimensionless parameters is in order here. In a high temperature plasma there are three lengths: \( \beta e^2 \) (average distance of closest approach), \( \kappa = \hbar/(2mkT)^{1/2} \) (thermal de Broglie wavelength), and \( \lambda_D = (4\pi \rho \beta e^2)^{-1/2} \) (Debye screening length). At high temperature these lengths are ordered as:

\[ \beta e^2 < \kappa < \lambda_D \]
Wave mechanical effects persist at high temperature because \( \kappa > \beta e^2 \); here high temperature means \( kT > \text{Ryd.} \) since \( \kappa = \beta e^2 \) when \( kT = \text{Ryd.} \). Partially ionized plasmas are at intermediate temperatures: \( kT \approx 5 \) or 10 eV. The interparticle spacing, \( \rho^{-1/3} \), need not be treated as a separate length since it is included in the Debye length. From these three lengths one may form two dimensionless parameters which suffice to describe the system; these are:

\[
\Lambda = \frac{\beta e^2}{\lambda_D} = \frac{1}{4\pi \rho \lambda_D^3} = 2^{1/2} \frac{e^3}{\beta^3} \rho^{1/2} \quad \text{--- classical plasma parameter or reciprocal of number of particles in the Debye sphere}
\]

\[
\gamma = \frac{\kappa}{\lambda_D} \quad \text{--- quantum diffraction parameter}.
\]

Statistical mechanicians can do analytic calculations for weakly interacting plasmas, which means essentially \( \Lambda \ll 1 \). At high temperature (\( kT > \text{Ryd} \)) our results are valid for \( \Lambda < \gamma < 1 \). Note that \( \Lambda^{2/3} = (4\pi)^{1/3} \beta e^2 \rho^{1/3} \sim \beta e^2 / \rho_o \). Thus the critical density defined by Prof. Ecker as the density for which \( \rho^{-1/3} \sim \lambda_D \), also means \( \rho^{-1/3} \sim \beta e^2 \) and hence \( \Lambda_{\text{critical}} \sim 1 \). Thus the weak coupling results which I will present are valid for \( \rho < \rho_{\text{critical}} \). This talk will proceed according to the following outline:

1. Electron gas (one component plasma; hence only repulsive Coulomb forces)
   a) \( \kappa = 0 \) (classical limit)
   b) \( \kappa \neq 0 \).

2. Two component plasmas, fully ionized, i.e. electrons and protons, obeying classical statistics, Maxwell-Boltzmann. (High temperature, low density).
3. Partially degenerate plasma; lower temperature and higher density so that Fermi-Dirac statistics are required.

4. Use of above results to give a statistical mechanical derivation of the "lowering of the ionization potential."

5. A proposed method for treating bound states in plasmas.

Hopefully (4) will be relevant to this meeting. I hope to demonstrate that by one definition of the "lowered ionization potential" that the best answer is:

a) \(-\frac{e^2}{\lambda_D}\) for \(\rho < \rho_{\text{critical}}\) and \(kT\) larger than a few volts

b) \(-\frac{e^2}{r_0}\) for \(\rho\) very large.

Thus I seem to disagree with Professor Ecker.

I. ELECTRON GAS

Suppose one tries to estimate the Coulombic interaction effects on the Helmholtz free energy from the second virial coefficient (the interaction between two particles), and furthermore one keeps only the first three terms in an expansion of the second virial coefficient in powers of \(\beta e^2/r\). The result is:

\[
\beta (F - F_\infty) = \beta F_1 = -\frac{N^2}{2!} \left[ \sum_0^\infty \frac{4\pi r^2 dr}{V} \left\{ \frac{1}{2!} \left( \frac{\beta e^2}{r} \right)^2 - \frac{1}{3!} \left( \frac{\beta e^2}{r} \right)^3 + \ldots \right\} 
\]

\[
= \frac{4\pi N_0}{2} \left[ \frac{1}{2} (\beta e^2)^2 L_{\text{max}} - \frac{1}{6} (\beta e^2)^3 \log \left( \frac{L_{\text{max}}}{\lambda_{\text{min}}} \right) + \ldots \right]
\]

(The term of \(O(\beta e^2/r)\) vanishes because of the electrical neutrality condition). The second line of the equation shows the divergencies produced in such an elementary incomplete approach. It is to be expected that a more complete calculation will give:
\[ L_{\text{max}} = \lambda_D \]

\[
\begin{align*}
\lambda_{\text{min}} &= \beta e^2 (\kappa << \beta e^2) \\
\lambda_{\text{min}} &= \kappa (\kappa > \beta e^2)
\end{align*}
\]

and this is what will happen. In order to describe the procedure diagrams are useful since they can be drawn much faster than lengthy integrals can be written. Diagrammatically the above equation is:

\[ \beta F_I = \frac{r_1}{r_2} + r_1 \frac{r_2}{\cdots} \]

where a point is the location of a particle and a line indicates a Coulomb interaction. In recent years due to the work of Meeran, Friedman, and Abe, and others it has been shown how to take the raw perturbation expansion for the Helmholtz free energy (i.e. simply all powers of \( e^2/r \)), group together systematically infinite series of terms and obtain a new expansion appropriate for the Coulomb gas. Basically one sums chains of Coulomb interactions to give the Debye screened potential to remove all long range divergencies \((L_{\text{max}} = \lambda_D)\), and sums powers of \( e^2/r \) between two particles to give the short range cut-off, \( \lambda_{\text{min}} = \beta e^2 \), which is appropriate to the classical problem. This procedure gives:

\[ \beta F_I = -N\left(S_{\text{ring}}(\Lambda) + \sum_{n=2}^\infty S_n(\Lambda) + \Lambda^2 G(n^2)\right) \]

where \( n = \frac{\kappa}{\beta e^2} = \frac{\gamma}{\Lambda} \).
Discussion of the quantum terms \( G(\eta^2) \) will be postponed for a few minutes.

The ring term is:

\[
S_{\text{ring}} = 1 \quad 2 + \quad 2 \quad 1 \quad 3 + \quad 2 \quad 3 + \quad 1 \quad 4 + \quad 2 \quad 4 + \quad 3 \quad 5 + \ldots
\]

\[0\left(\beta e^2 \rho L\right)^2 - 0\left(\beta e^2 \rho^2 L^3\right) + 0\left(\beta e^2 \rho^3 L^5\right) - \ldots\]

\[= \frac{\Lambda}{3}
\]

where the wavy line denotes the Debye potential:

\[
\varnothing = \varnothing \quad \rho \quad \lambda_D
\]

These funny diagrams describe the Montroll and Mayer (1950)\(^2\) derivation of Debye-Hückel result (1923)\(^3\) and establish that ring diagram are synonymous with Debye-Hückel. The intuitive methods used by Debye and Huckel cannot give higher order results, and it was only in 1959\(^1\) that the systematic procedure gave something beyond the Debye theory. The Abe \( S_2 \) is formally analogous to the second virial coefficients; it is the sum of three and more screened Coulombic interactions between two particles:

\[
S_2(\eta) = \sum_{m=3}^{\infty} \oint_{L} r^2 \, dr \, \sum_{m=3}^{\infty} \frac{(-\varnothing \rho)^m}{m!}
\]

where \( \varnothing = \frac{\beta e^2}{r} e^{-r/\lambda_D} = \frac{\Lambda}{x} e^{-x} ; \quad x = r/\lambda_D \)
\[ S_2(\Lambda) = \frac{(4\pi\rho\lambda^3)}{2} \int_0^\infty x^2 dx \{ \frac{\Lambda}{x} e^{-x} \} - 1 + \frac{\Lambda}{x} e^{-x} - \frac{1}{2} \left( \frac{\Lambda}{x} e^{-x} \right)^2 \]

\[ = \frac{\Lambda^2}{6} \left( \log \Lambda + D_1 \right) + \frac{3}{6} \left( \log \Lambda + D_2 \right) + \ldots \]

\[ D_1 = \log 3 + 2C - \frac{11}{6} \]

\[ D_2 = \log 4 + 2C - \frac{25}{12} \]

Generally \( S_n(\Lambda) \) describe all possible screened interactions among clusters of \( n \) particles. One finds that:

\[ S_3(\Lambda) = a\Lambda^3 + b\Lambda^4 (\log \Lambda + d) + \ldots \]

Thus far it looks like a nice expansion, but higher orders are not so encouraging; since \( S_4(\Lambda) \) is also of \( O(\Lambda^3) \) while \( S_5(\Lambda) \) and \( S_6(\Lambda) \) are of \( O(\Lambda^4) \). Not much can be said about the convergence of this expansion, but the lower order terms get smaller with larger \( n \), at least for \( \Lambda < 1 \).

For \( \Lambda > 1 \) this low density (small \( \Lambda \)) expansion is useless since the electron gas looks more like a liquid, i.e., \( \langle \text{Potential Energy} \rangle \sim \langle \text{Kinetic Energy} \rangle \). Numerical results obtained by a Monte Carlo procedure have become available this year for \( \Lambda \) of any value. At high enough density, i.e., \( \langle \text{P.E.} \rangle \gg \langle \text{K.E.} \rangle \) one expects the gas to crystallize into a lattice, and the computing machines at Livermore have verified this expectation. It is found that:

\[ BF \rightarrow - N C_M \frac{\Lambda^{2/3}}{M} \quad \text{for} \quad \Lambda > 2465 \]
Thus: \( F/N = -\frac{C_M e^2}{r_0} \) \( C_M \) = Madelung constant for body centered cubic lattice.

So far \( \eta \) has been assumed equal to 0. With \( \eta \neq 0 \) small quantum effects can be calculated from the Wigner-Kirkwood expansion\(^5\) (essentially a WKB procedure). The result is:

\[
G(\eta^2) = -\frac{\eta^2}{12} + \frac{\eta^4}{60} + \frac{\eta^6}{63} \ldots \text{valid for } \eta < 1
\]

where \( \eta = \frac{\varepsilon}{2e^2} = \frac{Y}{A} \). Evidently these low temperature wave mechanical effects are academic since they have nothing to do with the physics of a real two component plasma at intermediate temperature.

II. TWO COMPONENTS, HIGH TEMPERATURE

Such a high temperature plasma must be quantum mechanical to some extent since \( \varepsilon^2 < \varepsilon \) for \( kT > \text{Ryd} \). The calculation method either for one component or many components is to use the quantum generalization of the diagrammatic procedure used for the classical electron gas. The diagrams became more complicated in the quantum theory, however, since the particles can no longer be represented as points, but instead they propagate in inverse temperature "time" from 0 to \( \beta \). (We are solving the Bloch equation \( \frac{\partial \rho}{\partial \beta} = -\hat{H}_0 \), then \( \beta \) is analogous to \( it/\hbar \) in the Schröedinger equation.) For second order we have:
The quantum diagram says that two particles initially in momentum states $p_1$ and $p_2$ interact at time $\beta_1$, and are excited to states $p_1-q$ and $p_2+q$ leaving "holes" in the unperturbed momentum distribution indicated by arrows downward. The quantum mechanical ring diagram becomes:

$$S_{\text{ring}}(\Lambda, \gamma) = \begin{array}{c}
\begin{array}{c}
\text{Diagram}
\end{array}
\end{array} \text{ where } U_s(q, \omega) = \begin{array}{c}
\begin{array}{c}
\text{Diagram}
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{Diagram}
\end{array}
\end{array} + \ldots$$

$$U_s(q, \omega) = \frac{U(q)}{K(q, \omega)} \& U(q) = \frac{4\pi e}{q^2}$$

$$S_{\text{ring}}(\Lambda, \gamma) = \frac{\Lambda}{3} \left[ 1 - \frac{3\pi^{1/2}}{2^{5/2}} \gamma + \frac{1}{4} \gamma^2 \right] - \ldots$$

obtained by DeWitt and Sakakura (1960). The quantity $U_s(q, \omega)$ is the quantum generalization of the Debye potential. It is the four dimensional Fourier transform of $U_{\text{eff}}(r_{12}, t_1-t_2)$, the effective potential between plasma particles at point $r_1$ and time $t_1$, and a second particle at $r_2$ and $t_2$. $K(q, \omega)$ is the plasma dielectric function:

$$K(q, \omega) = 1 + U(q) \lambda(q, \omega)$$
and \( \lambda(q, \omega) = \bigg[ \bigg] = \) Fourier analysis of charge density fluctuations

\[
\lambda(q, \omega) = \int \frac{d^3 p}{(2\pi \hbar)^3} \frac{f(p) - f(p + q)}{(p + q)^2 - \frac{p^2}{2m} - \hbar \omega}
\]

in lowest order (random phase approximation).

For the next term beyond the ring diagrams one finds:

\[
S_{2, 3} = \frac{\lambda^2}{12} \left( - \log \frac{\lambda D}{\lambda} + D_Q + O(\gamma) \right)
\]

\( \xi \) a constant

(Two particles, three interactions).

The integrals represented by this diagram are quite lengthy, but have been recently evaluated at least to get the short range cut off at \( \xi_{\text{min}} = \xi \).

It is easy to show that the higher order diagrams are:

\[
S_{2, m} = \frac{(\beta e^2)^m}{\xi^{m-3}}
\]

and are thus negligible when \( \beta e^2 < \xi \).

The results for two components, \( N_e + N_i = N \), \( f_e = N_e / N \), \( f_i = N_i / N \), calculated as sketched above is:
\[ \beta F(\beta, \rho_e, \rho_i) = - N \left( S_{\text{exchange}} + \frac{\Lambda^2}{12} \left[ \log \frac{\kappa_{ee}}{\lambda_D} + D_Q \right] + 2 Z_e z_i^3 f_{f_i} (\log \frac{\kappa_{ei}}{\lambda_D} + D_Q) \right) \]

\[ + z_i^6 f_i^2 (\log \frac{\kappa_i^2 \beta e^2}{\lambda_D} + D_i) \]...

(The equation of state for a fully-ionized plasma)

valid when

\[ \kappa_{ii} < \beta e^2 < \kappa_{ei}, \kappa_{ee} < \lambda_D \]

\[ \text{(Ryd} < \kT < \frac{m_i}{m_e} \text{ Ryd}) \]

The ion-ion contribution is classical because of the large mass of ions; \( m_i/m_e \approx 2000 \). The exchange contributions are:

\[ S_{\text{exchange}} = \frac{1}{2S+1} \left[ \frac{\gamma^2}{2} - \frac{\pi^{1/2} \log^{-2}}{2^{5/2}} \gamma h + 6\Lambda^2 \right] \]

and are not especially important at high temperature and low density.

III. PARTIALLY AND COMPLETELY DEGENERATE PLASMAS

Fermi statistics becomes significant when the quantity \( \zeta = \rho \kappa^3 = (\kappa^3 \rho / (2\kT)^{3/2}) \) is greater than 1:
\[ \zeta << 1 \quad \text{(Maxwell-Boltzmann)} \quad \text{I} \]

\[ \zeta \approx 1 \quad \text{(partial degeneracy)} \quad \text{II} \]

\[ \zeta >> 1 \quad \text{(complete degeneracy)} \quad \text{III} \]

It is interesting to mark off on a temperature – density plane what regions can be calculated with present day statistical methods. The parameter \( \zeta \) will mark off regions of different degeneracy. For the strength of the interaction we need a generalized form of the plasma parameter:

\[
\Lambda_F = \frac{1}{4 \pi \rho} \frac{\langle P.E. \rangle}{\langle K.E. \rangle}
\]

\[
\lambda_F = \left( \frac{kT}{4 \pi e^2 \rho \theta(kT)} \right)^{1/2}
\]

\[
\theta(kT) = \frac{1}{N(\alpha)} \frac{\partial N(\alpha)}{\partial \alpha}
\]

\[
N(\alpha) = \sum_p \frac{1}{1+e^{-\alpha+\beta \epsilon_p}}
\]

When \( kT < \varepsilon_F \) (Fermi energy) then the degeneracy parameter \( \theta(kT) \) replaces \( kT \) by \( \varepsilon_F \) in the definition of the screening length. At zero temperature \( \lambda_F \) becomes the Thomas-Fermi screening length. For any plasma with \( \Lambda_F < 1 \) the ring sum plus first order exchange gives the Helmholtz free energy to good accuracy. We can indicate this region by plotting on the \( \rho \) versus \( T \) plane contours at constant \( \zeta \) and constant \( \Lambda_F \).
With \( \Lambda_F < 1 \), we have in the various regions:

I. \( \mathcal{G}_F \) = analytic results discussed previously

II. \( \mathcal{G}_F \) = numerical evaluation of \( S_{\text{ring}} \) by computing machines

III. Analytic results again possible

\[
F = N\epsilon_F \left( R_0(\phi) + \frac{kT}{e_F} \right)^2 R_1(\phi) + \cdots
\]

where \( \phi = \frac{4}{\pi} \frac{me^2}{\hbar F} \) \( \propto \frac{\rho}{a_o}^{1/3} = r_s \) (parameter used by solid state physicists)

\( \Lambda_F \propto \phi^{3/2} \)

\[
R_0(\phi) = \frac{3}{5} - \frac{3}{8} \phi - \frac{1}{3}(1 - \log 2)\phi^2 \log \phi
\]

\( \uparrow \) ideal gas 1st order exchange

\( \uparrow \) Gell-Mann and Bruechner results for the ring sum
\[ R_1(\phi) = \frac{\phi^2}{4} \left[ 1 - \frac{\phi}{8} \left( \log \frac{4}{6} - 2 \right) \right] . \]

Most laboratory plasmas, solar corona, ionosphere, etc. fall into region I. The electrons in metals fall into the difficult intermediate region \((2 < r_s < 5)\) where calculations cannot yet be done with any dependable accuracy. Stellar interiors like the sun are mostly in region II, white dwarfs in III. Very high pressure experiments on the earth, high energy shock waves and nuclear explosions, can compress light elements enough that they are in region III.

\[ \text{IV. AVERAGE ENERGY OF A FREE CHARGE IN A PLASMA} \]

With the results for free energy in mind we may now consider the derivation of the "lowering of the ionization potential". To illustrate the method consider the formal calculation of the average potential energy. We can write:

\[ Z(g) = \text{Tr} \ e^{-\beta (H_0 + g U)} = e^{-\beta F(g)} \]

where \( g \) is just equal to 1 at the end. One differentiation gives:

\[ \left( \frac{\partial F(g)}{\partial g} \right)_{g=1} = \frac{\text{Tr} \ U \ e^{-\beta H}}{\text{Tr} \ e^{-\beta H}} \]

Similarly fluctuations are given by the second derivation

\[ \left( \frac{\partial^2 F(g)}{\partial g^2} \right)_{g=1} = \frac{\partial^2 \beta F}{\partial g^2} \left. \right|_{g=1} \]
In the plasma problem we would like to know the average potential energy of a typical particle in a plasma. At any one instant this is:

\[ U_\alpha = z_\alpha \sum_{\beta \neq \alpha} \frac{z_\beta e^2}{r_{\alpha\beta}}. \]

We can calculate the average value of \( U_\alpha \) from the free energy just by differentiating with respect to \( z_\alpha \), and putting it to its actual value at the end. Thus:

\[ \langle \beta U_\alpha \rangle = \left( \frac{z_\alpha}{z_\alpha} \right) \sum_{\beta < \alpha} \frac{z_\beta e^2}{r_{\alpha\beta}} \cdot -\beta (H_0 + \sum_{\beta < \alpha} \frac{z_\alpha z_\beta e^2}{r_{\alpha\beta}}) \]

To use this formal expression we simply need to distinguish the particle charges in the various forms of the dimensionless parameters, and differentiate the free energy expression. Thus:

\[ \Lambda = \Lambda \left( \sum_{j=1}^{N} \frac{z_j^2}{\langle z^2 \rangle_N} \right)^{3/2} \]

\[ \frac{\partial \Lambda}{\partial z_\alpha} = \frac{3z_\alpha}{\langle z^2 \rangle_N} \Lambda \]

and similarly for the zero temperature parameter:

\[ \phi = \phi \left( \sum_{j=1}^{N} \frac{z_j^2}{\langle z^2 \rangle_N} \right) \]

\[ \frac{\partial \phi}{\partial z_\alpha} = \frac{2z_\alpha}{\langle z^2 \rangle_N} \phi \]

For a plasma in Region I (high temperature and low density) we find:
\[
\langle \beta U_\alpha \rangle = - \frac{\beta Z_\alpha^2 e^2}{\lambda_D} \left\{ 1 + \frac{\Lambda}{2} \left[ Z_\text{e}^6 e^2 \left( \log \frac{\chi_{ee}}{\lambda_D} + D_0 \right) \ldots \right] \right\}.
\]

If particle \( \alpha \) is an electron then \( U_\alpha \) is one definition of the lowering of the ionization potential, \( \Delta \chi \); that is, even for an electron sitting still in the plasma, the energy \( e^2/\lambda_D \) must be supplied to remove it to infinity. For low density (\( \Lambda \ll 1 \)) the Abe corrections in the above equation becomes negligible, and the result is simply:

\[
\langle U_\alpha \rangle = - \frac{Z_\alpha^2 e^2}{\lambda_D}.
\]

These expressions are just as good as our free energy expression.

For matter at extremely high density the free energy expression of region III is appropriate, and one finds:

\[
\langle U_\alpha \rangle = - \frac{3}{4} \varepsilon F \phi (1 - \frac{2}{3} (1 - \log 2) \phi \log \phi \ldots) \]

\[
= -1.48 e^2 \rho^{1/3} (1 - \ldots).
\]

Thus for \( \Delta \chi = \langle U_\alpha \rangle \) we get essentially the ion sphere model \( - e^2/r_\alpha \), from the first order exchange term. This is a rigorous high density result, though the density intended (to make \( \phi < 1 \)) is probably much higher than what Stewart and Pyatt intended in their work with the ion sphere model.

V. BOUND STATES

The systematic rigorous theory of partially ionized plasmas is unfortunately far from being developed to a practical extent. Eventually,
no doubt, theoretical physicists will be able to start with $N_e$ electrons
and $N_1$ point nuclei, and calculate accurately the thermodynamic properties
even when a considerable fraction of the electrons are bound. My attempts
in this direction have been slightly encouraging, but not yet very useful.
Even so I will use my approach for a short discussion of bound states, and
the question of what $\Delta \chi$ should be.

In the diagrammatic expansion of the two component partition function
one knows already just where hydrogenic atoms should appear, namely, the
quantum form of the Abe $S_2$ integral, i.e., the sum of ladder interactions
between an electron and a point ion:

$$S_{2,ei} = \sum_{m=3}^{\infty} \frac{1}{m!} \left( \frac{x}{\lambda} \right)^m$$

Recall that for $kT > \text{Ryd}$ there are not bound states, and the leading term
of this sum, $m = 3$, can be evaluated to give $\frac{1}{12} (x \log \frac{e_i}{\lambda})$. For the
intermediate temperatures, $kT < 5 \text{ eV}$, all the ladders must contribute. This
quantity, $S_{2,ei}$, resembles the quantum second virial coefficient, and some
analysis similar to the Beth-Uhlenbeck work is possible. One can show that
the ladder diagram sum may be expressed as:

$$S_{2,ei} = \beta \left[ \frac{dZ}{2\pi i} e^{-\beta Z} \text{Tr} \left( Z - (H_0 + U_s(Z)) \right) \right]$$

where $Z$ contour encloses the real axis, and $U_s(Z)$ is the quantum dynamic
screened potential defined earlier. The eigenvalues of the operator $H_o + U_s(E)$
should be the bound state energies of an electron-ion system moving in a
plasma. Suppose we just concentrate on getting these eigenvalues. Then we
have to solve a Schröedinger-like equation:
\[(H_0 + U_s(E_n))\psi_{n\ell} = E_{n\ell} \psi_{n\ell}\]

in which the potential, \(U_s(E) = \frac{U_c}{K(E)}\) incorporates the many body effects of the plasma medium in the plasma dielectric function. It is then convenient to divide the screened potential into the pure Coulomb part and a polarization part:

\[U_s(k,\omega) = \frac{U(k)}{K(k,\omega)} = U(k) + U_p(k,\omega)\]

Therefore \(U_p(k,\omega) = U_s - U = U(k) \frac{1}{K(k,\omega)} - 1\).

In the static limit, \(\omega = 0\), this screened potential becomes just the familiar Debye potential, \(U_s(k,0) = 4\pi e^2/(k^2 + \lambda_D^{-2})\) or \((e^2/r)e^{-r/\lambda_D}\) in configuration space. The static case has been worked out by Harris. 11

The more complete dynamic potential, however, has in it important dynamic effects. Since \(K(k,\omega)\) has real and imaginary parts, one finds that the energy eigenvalues are complex, \(E_{n\ell} = E_{n\ell}^0 + \delta E_{n\ell} + i \Gamma_{n\ell}\) where \(E_{n\ell}^0 = -\text{Ryd}/n^2\), \(\delta E_{n\ell}\) is a shift away from the Rydberg spectrum, and \(\Gamma_{n\ell}\) is interpreted as the reciprocal lifetime of the state labelled by \(n\ell\). This equation can be written in explicit form only in momentum space, and unfortunately little is known about solving it. An attempt has been made by noting that the polarization potential \(U_p\) is proportional to the plasma density, so that at least for the low lying energy levels \(U_p\) should be a small perturbation, and one should be able to calculate the shift and width of each level from;
\[ \delta E_{nl} + i \Gamma_{nl} = (\psi_{nl}^0 U \psi_{nl}^0) \]

where \( \psi_{nl}^0 \) are Coulombic wave functions. Results have been obtained using for \( K(k, \omega) \) the first approximation (the random phase approximation), but these results have little to do with real plasmas because of the approximation. Nevertheless the method is probably correct and may someday yield good results.

Note that the method described should be considerably better than using simply the energy levels for the static Debye potential (work of G. Harris).

Note that the static limit potential may be expanded in powers of \( r \) as
\[
\left( e^2/r \right) e^{-r/\lambda_D} = e^2(1/r - 1/\lambda_D + \frac{1}{2} r/\lambda_D^2 \ldots )
\]
and one sees that in this simple model every level is shifted upwards by the amount \( e^2/\lambda_D \); there is a smaller dipole shift downward. Thus this model would say that the ionization potential is changed by \( 2 e^2/\lambda_D \), which seems improbable. By using the nonstatic potential \( U_s(k, \omega) = U(k)/K(k, \omega) \), it is hard to yet calculate any accurate value of the shift of the lower levels, but the conclusion of my work is that the lower levels are shifted hardly at all. Thus I agree with the conclusion of Klein and Jackson.

In this diagram is shown the Rydberg spectrum for hydrogenic atoms and ions for vacuum and for a plasma. The plasma in which the atom is moving shifts the levels, perhaps significantly near the top. Probably, the more important effect, however, is the broadening of the levels (the \( \Gamma_{nl} \) mentioned before).
Somewhere near the top, and usually below $-e^2/\lambda_D$, the levels are so broadened that they can no longer be resolved. Electrons in such bound states may then look free for some experiments. I can't say where the levels merge due to broadening. Perhaps Professor Ecker's results of $-e^2/r_0$ for $\Delta \chi$ is meant to describe this effect.

It was pointed out by Dr. Hochstim that perhaps the nearby bound electrons in these upper levels that overlap below $-e^2/\lambda_D$ may be able to move from nucleus to nucleus in much the same manner as conduction electrons in metals. If so they might be mobile enough to be "free" electrons for d.c. conductivity measurements, but "bound" for microwave absorption measurements. Theoretical calculations are very incomplete on this point. It is my impression that for use in the Saha equation these electrons below $-e^2/\lambda_D$ should be regarded as bound, and the cut off $\Delta \chi$ should be taken at $-e^2/\lambda_D$. 
REFERENCES


H. L. Friedman, Ionic Solution Theory Based on Cluster Expansion Methods,


A. Y. Sakakura, The Connected Diagram Expansion of the Grand Partition
Univ. of Colorado 1960.


9. T. Nakayama and H. DeWitt, J. of Quant. Spectroscopy and Radiative Transfer,

10. Hirschfelder, Curtiss, and Bird, Molecular Theory of Gases and Liquids,

V. THOMAS-FERMI METHODS IN THE DESCRIPTION OF THE
PLASMA IN EQUILIBRIUM

John C. Stewart*†

and

Kedar D. Pyatt, Jr.

General Atomic Division, General Dynamics Corporation
John Jay Hopkins Laboratory for Pure and Applied Science
San Diego, California

ABSTRACT

The average electrostatic potential near a nucleus immersed in a plasma is evaluated using a finite-temperature Thomas-Fermi model. The part of this potential directly attributable to the presence of the plasma is isolated and is used to evaluate the reduction in ionization potential for a wide range of parameters. A simple analytic solution, exhibiting Debye-Hückel and ion-sphere limits, is also obtained and is used as an interpolatory device.

* Paper presented by John C. Stewart.
In a plasma of finite density the potential distribution in and near a given ion is influenced not only by its own bound electrons, but also by free electrons, by neighboring ions, and (slightly) by neutral atoms. These perturbers produce effects of two kinds: their time-averaged effect is to alter the set of energy levels available to the ion in question, and their time-dependent effect is to broaden these levels both by shifting them back and forth adiabatically and by inducing transitions between them. The first effect, besides providing a natural cutoff to the bound-state partition function, effectively lowers all the ionization potentials and shifts the equilibrium occupation numbers in the direction of increased ionization. This effect, which is most important at high densities, is usually called "pressure ionization." The second effect, "pressure broadening," is not considered in this paper.

Pressure ionization has often been treated by assigning to each ion a sphere occupying the ion's share of the total volume and containing the ion and enough free electrons to make the sphere's net charge zero (Mayer 1947, Armstrong, et al., 1961). In the simplest form of this "ion-sphere" approach, the free-electron density is assumed spatially uniform. Inside the sphere the potential due to the contents of neighboring spheres is neglected. Thus, close encounters between ions are disregarded, and the picture is basically that of a crystal lattice, with strongly correlated ion positions. This strong positional correlation between ions (though not necessarily the uniform free-electron density) may be expected to hold at high densities and at low temperatures. At the opposite extreme is the
case of nearly random ion positions; the first-order deviation from randomness leads to the Debye-Hückel potential (Debye and Hückel 1923; Griem 1964), which is valid in the low-density, high-temperature limit. In this paper we develop a theory of pressure ionization which yields the ion-sphere and Debye-Hückel results as approximate limiting cases, and provides results over essentially the entire range of temperatures and densities for which appreciable ionization exists and the free electrons are nondegenerate.

Our starting point is the finite-temperature Thomas-Fermi (TF) model for the electrons, which has previously been employed (Marshak and Bethe 1940; Feynman, Metropolis, and Teller 1949; Latter 1955) to calculate the equation of state of high-temperature, high-density material. In these calculations the entire electron distribution was described as a Fermi gas divided into ion spheres, and the resulting equation of state shows no effects of atomic shell structure. Keller and Meyerott (1952) extended the model to include the ions in the vicinity of a given nucleus, thus relaxing the "frozen" nuclear positions of the ion-sphere model; they solved the resulting differential equation for the total potential numerically, subtracted the potential of the nucleus and inner electrons, and interpreted their results in terms of the perturbing potential experienced by bound electrons in various shells, i.e., the lowering of the ionization potential for each shell. Expressing the interactions between bound electrons in terms of screening constants, they then obtained the average occupation number for each shell as a function of temperature and density, using the perturbed binding energies. However, their treatment appears to include twice the interaction of a given bound electron with all bound electrons located further from the nucleus: once in the perturbing potential, and once in the screening constants. Consequently they obtained marked differences
from shell to shell in the "effect of the surrounding plasma on the ionization potential," since these outer bound electrons were in effect included as part of the "surrounding plasma."

Accordingly, we have reformulated the model so as to isolate the potential due to the free electrons and neighboring ions; a free electron is one with sufficient energy to escape to infinity in the plasma. It is this potential which we identify with the "effect of the surrounding plasma," regarding the bound electrons as part of the unperturbed ion; one result is that the perturbing potential is practically the same for all bound electrons except highly excited ones.

An essential physical limitation of the model is its neglect of fluctuations; only time-averaged, spherically-symmetric potential and charge distributions are considered. Thus near a given "central" ion the position correlation between each perturber and the central ion is taken into account, as is the correlation between each perturber and the "mean" distribution of the other perturbers, but the correlation between individual perturbers is neglected. This neglect is shown by Keller and Meyerott (1952) to be justified in the case of a multiply-charged central ion surrounded by perturbers of smaller charge—e.g., in the astrophysically important case of a stellar mixture consisting mostly of hydrogen and helium in which the ionization potential of a heavy ion is sought. In other circumstances the validity of the model has not been proven, so our results are perhaps provisional; however, because of the relationship of the present model to the simpler treatments mentioned above, we have considered it illuminating to cover a large parameter range for comparison purposes.
II. FORMULATION

Consider a nucleus $Z$ fixed in a sea of electrons and point ions (we neglect the influence of neutral atoms) at a kinetic temperature $T$. We wish to find the time-averaged potential distribution around $Z$, and we assume for the present that only this average is felt by any one particle; that the potential distribution is spherically symmetric around $Z$; that is determined by the time-averaged, spherically symmetric charge density; and that it changes only slightly within one particle wavelength. We describe the electrons by nonrelativistic Fermi-Dirac statistics and the ions by nonrelativistic Maxwell-Boltzmann statistics. These assumptions are those of the finite-temperature TF atomic model, extended to include the neighboring ions. The electrostatic potential $\Phi(r)$ is then determined by the Poisson equation

$$\nabla^2 \Phi = \frac{1}{r} \frac{d}{dr} \left( r \frac{d}{dr} \Phi(r) \right) = -4\pi \epsilon \sum_{i} z_i n_i - n_e,$$

where $n_e$ is the local number density of electrons, $n_i$ is the local number density of ions of charge $e z_i$, and

$$n_e(r) = \int_0^\infty n(t) dt = n_e(\infty) \frac{F[\epsilon(r) - \alpha]}{F(-\alpha)}, \quad n_i(r) = n_i(\infty) \exp \left(-z_i \frac{\epsilon(r)}{kT} \right),$$

$$F(\eta) = \int_0^\infty \frac{t^{1/2}}{e^{-\eta} + 1} dt, \quad \Phi(\infty) = 0, \quad r \Phi + Z e \text{ as } r \to 0.$$

The degeneracy parameter $\alpha$ is related to the free-electron density far from the ion $n_e(\infty)$ by
\[ n_e^{(\infty)} = \frac{2(2\pi mkT)^{3/2}}{h^3} \frac{2}{\sqrt{\pi}} F(-\alpha) \]

In these equations \( t \) is essentially the kinetic energy parameter \( (t = p^2/2mkT) \), so that for Fermi-Dirac statistics \( n(t)dt = (4\pi/h^3)(2\pi mkT)^{3/2} (t^{1/2}dt/e^{\alpha-y+t}+1) \). We consider only applications where \( \alpha \) is positive and appreciably larger than unity; i.e., the density is sufficiently low that the free electrons are nondegenerate, and

\[ \frac{2}{\sqrt{\pi}} F(-\alpha) \sim e^{-\alpha} \ll 1 \]

Close to the nucleus, where \( e\phi > akT \), there is a region of degenerate bound electrons which is, in fact, the ion core. The asymptotic ion densities \( n_i^{(\infty)} \) satisfy the condition of electrical neutrality, \( \sum_i z_i n_i^{(\infty)} = n_e^{(\infty)} \).

Under the substitutions

\[ y = \frac{e\phi}{kT}, \quad x = \frac{r}{D}, \quad \frac{1}{D^2} = \frac{4\pi e^2}{kT} \sum_i (z_i^2 + z_i) n_i^{(\infty)} \]

(note that \( D \) is the Debye length including ions and electrons), the above equations take the nondimensional form

\[ \frac{1}{x} \frac{d^2}{dx^2} (xy) = \frac{1}{z^* + 1} \left[ \frac{F(y-\alpha)}{F(-\alpha)} - \frac{\langle z \exp(-zy) \rangle}{\langle z \rangle} \right] \]

where \( \langle \rangle \) denotes an average, weighted with \( n_i^{(\infty)} \), over ion species, and \( z^* = \frac{\langle z^2 \rangle}{\langle z \rangle} \). The second term on the right side may be simplified with small loss of accuracy by noting that it is comparable with the first only for fairly small \( y \); in this region,

\[ \frac{\langle z \exp(-zy) \rangle}{\langle z \rangle} = \frac{\langle z(1 - zy + \ldots) \rangle}{\langle z \rangle} = 1 - z^* y + \ldots = e^{-z^* y} \]
so that to this approximation the assortment of ion species present can be replaced by a single fictitious species with charge $z^*$; $z^*$ is never less than unity, even when $\langle z \rangle \to 0$. Our basic equation for the potential distribution is then

$$\frac{1}{x} \frac{d^2}{dx^2} (xy) = \frac{1}{z^* + 1} \left[ \frac{F(y - \alpha)}{F(-\alpha)} - \exp(-z^* y) \right], \quad (1)$$

with boundary conditions $y(\infty) = 0$ and $xy + Ze^2/(DkT) \equiv K_0$ as $x \to 0$.

Up to this point, our development is essentially the same as that of Keller and Meyerott (1952). Our treatment differs from theirs in the development which follows; we do not consider bound electrons as contributing to the pressure lowering of the ionization potential, since the bound electrons are already present in the isolated ion.

We do not want to treat the ion whose nucleus is $Z$ entirely by the TF model, but we want to isolate and evaluate the effect of the free electrons and neighboring ions on the potential distribution. Since the density distribution of these perturbers depends somewhat on the bound-electron distribution, we must assume a bound-electron distribution in order to find the free-electron distribution and the neighboring ion distribution. Having done so by means of the TF model, which approximates the average bound-electron distribution, we may apply this same perturbing potential to better models for the unperturbed bound-electron states, such as those of the isolated ion.

The perturbing potential $\Phi_f$ satisfies a Poisson equation in which only the free-electron and ion densities appear, and in dimensionless form this equation is
\[
\frac{1}{x} \frac{d^2}{dx^2} (xv) = \frac{1}{z+1} \left[ \frac{F(y-\alpha, y)}{F(-\alpha)} - e^{-z y} \right], \quad (2)
\]

where \(v = e^{\phi_f}/kT\) and \(F(y-\alpha, y) = \int_y^\infty (t^{1/2})/(e^{t+y}+1) dt\). (Note that \(F(y-\alpha, y)/F(y-\alpha)\) is the ratio of free-electron density to total electron density in the TF model; we define a free electron as one whose kinetic energy exceeds \(\epsilon_{\Phi}\) i.e., \(t > y\), and therefore \(n_f = \int_y^\infty n(t) dt\). Unlike \(y(x)\), which contains the nuclear potential, \(v(x)\) is finite at the origin, and \(v'(0) = 0\).

If we choose the zero of potential such that \(v(\infty) = 0\), \(v(x)\) will be negative; we let \(-v(0)\) equal \(J\). Then

\[
v(x) = -J + \int_0^x S(t) t dt - \frac{1}{x} \int_0^x S(t) t^2 dt, \quad (3)
\]

where \(S(x)\) is the right-hand side of Eq. (2), containing the solution \(y(x)\) of equation (1). Hence, \(J = \int_0^\infty S(x) x dx\). We can put equation (3) in a more convenient form:

\[
v(x) = -\frac{1}{x} \int_0^\infty S(t) t^2 dt + \frac{1}{x} \int_x^\infty S(t) t^2 dt - \int_x^\infty S(t) t dt, \quad (4)
\]

in which the first term, dominant at large \(x\), may be identified as the asymptotic Coulomb potential of the total excess of free electrons over neighboring ions. It will be seen shortly that the total potential \(y(x)\) vanishes exponentially at large \(x\). Now the potential due to the nucleus and bound electrons alone, \(y(x) - v(x)\), has an asymptotic Coulomb form which depends only on the net ionic charge; this observation permits us to find the net ionic charge in terms of \(\int_0^\infty S(t) t^2 dt\).
In the solution of the foregoing equations, the following expansions (Keller and Penwick 1953) are useful; they are valid when \( a \) is somewhat larger than unity, so that \( e^a \gg 1 \) and the free electrons are nondegenerate (only this case is treated in what follows):

\[
\frac{F(y - \alpha)}{F(-\alpha)} = \begin{cases} 
    e^y [1 - 2^{-3/2} e^{-\alpha}(1 - e^{-y}) + \ldots] & \text{ }(y \ll \alpha) \\
    \frac{4}{3\sqrt{\pi}} e^\alpha (y - \alpha)^{3/2} \left[ 1 + \frac{\pi^2}{8(y - \alpha)^2} + \ldots \right] & \text{ }(y \gg \alpha),
\end{cases}
\]

\[
\frac{F(y - \alpha, y)}{F(-\alpha)} = 2\sqrt{\frac{\alpha}{\pi}} + e^y (1 - \text{erf} \sqrt{y}) = \begin{cases} 
    2\sqrt{\frac{y}{\pi}} \left[ 1 + \frac{1}{2y} - \frac{1}{4y^2} + \ldots \right] & \text{ }(y \gg 1) \\
    1 + y + \frac{4}{3\sqrt{\pi}} y^{3/2} + \frac{1}{2} y^2 + \ldots & \text{ }(y \ll 1),
\end{cases}
\]

From these and the form of equation (1), we can distinguish four regions of progressively smaller \( x \) (larger \( y \)).

Region A. The limiting form of equation (1) for large \( x \), where \( y \ll 1/z^* \), is

\[
\frac{1}{x} \frac{d^2}{dx^2} (xy) = y
\]

with the solution \( y = (C/x) e^{-x} \), which is the form of the Debye-Hückel potential. In the region where this holds, the charge densities of ions and electrons nearly cancel, and most of the electrons are free.
Region B. Proceeding inward, if \( z^* \gg 1 \), there is a region where
\( 1/z^* << y << 1 \); and the densities of the ions and of the bound electrons are
small compared with that of the free electrons, which is approximately
constant and equal to its asymptotic value. In this region, equation (1)
becomes approximately
\[
\frac{1}{x} \frac{d^2}{dx^2} (xy) = \frac{1}{z^* + 1}
\]
with the solution
\[
y = \frac{A}{x} + B + \frac{x^2}{6(z^* + 1)}
\]
in which \( A \) and \( B \) are arbitrary constants which must be fixed by
boundary conditions. The ion-sphere model with uniform free electrons
yields a solution of this form.

Region C. In the next region, \( 1 << y << \alpha \), the bound electrons
outnumber the free, but the occupation of the bound states is well below
their capacity; and the local kinetic-energy distribution is still
approximately Maxwellian. The free-electron density is now larger than its
asymptotic value. Here,
\[
\frac{1}{x} \frac{d^2}{dx^2} (xy) = \frac{1}{z^* + 1} e^y
\]

Region D. Finally, in the ion core, \( y \gg \alpha \) and most of the electrons
are in fully occupied states. Equation (1) becomes approximately the zero-
temperature TF equation. As the nucleus is approached, the bound-electron
density diverges as $x^{-3/2}$ and the free-electron density as $x^{-1/2}$ (fictions peculiar to the TF model); the total potential $y(x)$ approaches $K_0/x + \text{const.} + O(x^{1/2})$, and the perturbing potential $v(x)$ approaches $-J + O(x^{3/2})$.

The procedure for obtaining $v(x)$ should now be clear. There are basically three parameters in the problem: $z^*$, $\alpha$, and $K_0$. More convenient than the last of these, for purposes of inward integration, is $C$, the normalization constant of the solution in region A. We can choose $z^*$, $\alpha$, and $C$, integrate equation (1) inward to get $y(x)$ and hence $S(x)$, and obtain $v(x)$ from equation (4). The net ionic charge $z$ is given by

$$-\lim_{x \to \infty} x v(x) \to \frac{z e^2}{D k T} \equiv K = \int_0^\infty S(t) t^2 \, dt ,$$

and we recall that the perturbing potential at the origin is found from

$$-v(0) \equiv J = \int_0^\infty S(t) \, dt .$$

In application to a specific case, there are four physical parameters: $T$, $z^*$, and $\alpha$ for the plasma, and the net charge of the central ion. We take $z$ as the net charge after ionization; e.g., $z = 1$ refers to the process of removing an electron from a neutral atom. We evaluate the lowering of the ionization potential by imagining that the radial Schrödinger equation for a particular orbital is solved twice: once in the total potential due to all electrons and ions, and once in the unperturbed potential produced by the nucleus and bound electrons. In units of $k T$ the first potential is
y(x) and the second is \( y(x) - v(x) \); the difference between the resulting energy eigenvalues gives the lowering and can be evaluated from first order perturbation theory. Thus, given \( T, z^*, \alpha, \) and \( z \), the quantity \( -\bar{v} \) measures the lowering of the ionization potential in units of \( kT \), where \( -\bar{v} \) is the quantum mechanical expectation value of \( -v(x) \) averaged over the orbital from which the electron is being removed. Higher orders contribute nothing if \( v(x) \) is approximately constant where the orbital has appreciable amplitude, and, as we will see later this condition is closely approximated for all orbitals except the highly excited ones. The lowering \( (-\bar{v}) \) is therefore closely equal to \( J ( = -v(0)) \). What is usually needed, then, is \( J \) for prescribed \( T, z^*, \alpha, \) and \( z \). Our dimensionless formulation replaces \( T \) and \( z \) by the single parameter \( K \); the numerical results show that \( J \) is practically independent of \( \alpha \) for fixed \( z^* \) and \( K \); and the resulting interpolation problem for \( J \) as a function of \( z^* \) and \( K \) can be simplified by means of an approximate but physically suggestive solution, which we discuss in the following section.
III. APPROXIMATE SOLUTION

A very simple approximate solution for equations (1) and (4) is readily obtained by assuming that only regions A and B need be considered, i.e., that an adequate approximation to the perturbing potential is obtained by placing all the bound electrons at the origin and taking the free-electron density to be approximately uniform. Then equation (1) is just

$$\frac{1}{x} \frac{d^2}{dx^2} (xy) = \frac{1}{z^*+1} [1 - e^{-(z^*+1)y}]$$

For large $z^*$ we approximate the right side by

$$y \quad \text{when } (z^*+1)y < 1 \quad \text{(region A)},$$

$$\frac{1}{z^*+1} \quad \text{when } (z^*+1)y > 1 \quad \text{(region B)};$$

and letting $x_1$ denote the transition point, we require the potential and its derivative to be continuous at $x_1$. At small $x$, $y \to (K/x) - J + \ldots$, where to this approximation the first term is the Coulomb potential of the central ion, and the next is the perturbing potential evaluated at the origin, i.e., the reduction in ionization potential (in units of $kT$) produced by the free electrons and neighboring ions. Using the solutions in regions A and B, which are, respectively,

$$y = \begin{cases} \frac{C}{x} e^{-x} & (x > x_1) \\ \frac{K}{x} - J + \frac{x^2}{6(z^*+1)} & (x < x_1) \end{cases}$$
and the continuity conditions

\[ -x_1 = K - J x_1 + \frac{x_1^3}{6(z^* + 1)} \]

\[ -x_1 = J - \frac{x_1}{2(z^* + 1)} \]

we get

\[ J = \frac{x_1}{z^* + 1} \left( 1 + \frac{x_1}{2} \right) = \frac{1}{2(z^* + 1)} \left[ (x_1 + 1)^2 - 1 \right] \]

\[ K = \frac{x_1}{z^* + 1} \left( 1 + x_1 + \frac{x_1^2}{3} \right) = \frac{1}{3(z^* + 1)} \left[ (x_1 + 1)^3 - 1 \right] \geq J \]

or, eliminating \( x_1 \),

\[ J = \left( \left[ 3(z^* + 1)^{2/3} - 1 \right] / [2(z^* + 1)] \right)^{3/2} \]

(5)

which for small \((z^* + 1)K\) becomes \( J = K \), and for large \((z^* + 1)K\) becomes \( J = \left[ 2(z^* + 1)^{-1} [3(z^* + 1)K]^{2/3} \right] \). Defining the ion-sphere radius \( a \) for an ion of net charge \( z \) by the usual convention \( 4\pi a^3/3 = z/n_e(\infty) \) and recalling the expression for the Debye length \( D \),

\[ \frac{1}{D^2} = \frac{4\pi e^2}{kT} (z^* + 1) n_e(\infty) \]

we see that the parameter \( 3(z^* + 1)K \) is just

\[ 3(z^* + 1) \frac{z e^2}{D k T} = \frac{3z}{4\pi D^3 n_e(\infty)} = \left( \frac{a}{D} \right)^3 = \frac{\text{ion sphere volume}}{\text{Debye sphere volume}} \]
When this parameter is small,

\[ J + \frac{z e^2}{D kT} = K \]

when it is large,

\[ J + \frac{3}{2} \frac{z e^2}{akT} \]

These values of \( J \) are, respectively, the results of the Debye-Hückel and ion-sphere models, which result if one retains only region A or only region B a priori. Very roughly, one may say that the model giving the smaller depression of the ionization potential is the closer to the truth. (The prescription, which has sometimes been employed, of applying the sum of the corrections corresponding to the two models thus can seriously overestimate the depression of the ionization potential.)

Ecker and Kröll (1963) have derived an approximate result resembling our equation (5) in yielding Debye-Hückel and ion-sphere limits, but their ion-sphere radius is independent of \( z \), giving \( J \propto z \). Our result, in contrast, gives \( J \propto z^{2/3} \) in the ion-sphere limit, corresponding to an ion-sphere radius proportional to \( z^{1/3} \)—which is consistent with electrical neutrality of the sphere.
IV. NUMERICAL SOLUTIONS

In order to obtain values of \( J \) which are more accurate than those provided by equation (5), we have solved equation (1) numerically and evaluated \( v(x) \) from equation (4) for a number of values of \( z^* \), \( \alpha \), and \( C \). The calculations were executed on an IBM-7044 digital computer; equation (1) was replaced by a difference equation which was solved inward from large \( x \). Automatic mesh adjustment was employed to handle the steep behavior of \( y(x) \) near the origin. The complete Fermi-Dirac function \( F(y-a) \) was replaced by Arpigny's (1963) accurate polynomial representation; the incomplete function \( F(y-a,y) \) was replaced by the error-function approximation (Keller and Fenwick 1953) noted in Section II. The integrals in equation (4) were then evaluated by Simpson's rule. For each \( z^* \), \( \alpha \), and \( C \), the output included the values of \( K \), \( K_o \), and \( J \), and tables of \( y(x) \) and \( v(x) \). The quantity

\[
F = 2(z^* + 1)J \left\{ \left[ 3(z^* + 1)K + 1 \right]^{2/3} - 1 \right\}^{-1}
\]

was also computed (\( F \) is the ratio of \( J \) to the approximate \( J \) given by equation (5)) in order to facilitate interpolation; \( K \) and \( J \) range through several orders of magnitude, but \( F \) is of the order of unity. The calculations covered the range \( 1 \leq z^* \leq 100; \ 2 < \alpha < 12; \ 10^{-4} < K < 3; \) this range, we think, covers all possible cases of interest in nondegenerate LTE (local thermodynamic, equilibrium) plasmas. Some calculations in this range led to \( K_o/K = (\text{nuclear charge/net ionic charge}) > 103 \) and were accordingly rejected as unphysical; these occurred for \( C \) and \( \alpha \) both large. Since large \( C \) generally corresponds to high density and large \( \alpha \) to low density,
it is not surprising that prescribing both quantities can lead to physically unrealizable cases.

We first discuss the behavior of $J$ as a function of $z^*$, $\alpha$, and $K$. In Figure 1 we plot the correction factor $F$ against $(z^* + 1)K$ with $z^*$ as a parameter. The dependence of $F$ on $\alpha$ is all included in the shaded areas and so is generally negligible. (In terms of the qualitative discussion in Section II, this means that region D is an insignificant contributor to the perturbing potential; i.e., very few free electrons are found inside the ion core.) The overall closeness of $F$ to unity shows that the simple equation (5) is usually a fairly good approximation, especially for large $z^*$; however, better values of $J$ can be obtained from Figure 1.

We consider next the shape of the perturbing potential $v(x)$. If $v(x)$ were independent of $x$ throughout the volume where $y(x) \geq Y$, then all orbitals whose (depressed) ionization potentials exceed $YkT$ would experience essentially the same perturbation of their various ionization potentials, since their classical turning points lie inside the constant-$v$ region and their wave functions are small outside it. Similarly, because $v(x)$ is monotonic in $x$, the expectation value of $v(x)$ for a given orbital will be (approximately) bounded by the values of $v(x)$ at the outer turning point and at the origin; and at the outer turning point $y(x) \geq I/kT$ with $I = \text{perturbed ionization potential}$. Orbitals for which $v(x) \leq v(0)$ where $y(x) = I/kT$ accordingly have $-\bar{v}$, the depression of the ionization potential in units of $kT$, closely equal to $J$. We therefore ask for the behavior of $v(x)/v(0)$ as a function of $y(x)$. Two specific values of $y$ are of particular interest: $y = \alpha$, which corresponds roughly to the
outermost orbital in the ground state of the ion; and the value of \( y \) for which \( \nu(x) = 0.9 \nu(0) \), which corresponds roughly to the highest excited orbital for which \( JkT \) is a close (few-percent) approximation to the depression of the ionization potential. We find in nearly every case which we have computed that \( \nu(x) \) deviates from \( \nu(0) \) by considerably less than 1% where \( y(x) = \alpha \), and that \( y(x) \) is considerably less than unity where \( \nu(x) = 0.9 \nu(0) \). Therefore, the perturbing potential is indeed nearly constant for any orbital whose depressed ionization potential exceeds \( kT \) (and the wave function of such an orbital will be essentially the same as in the isolated ion).

The highly excited orbitals with \( I \ll kT \) can be neglected in most applications such as calculation of the LTE equation of state of the plasma, since it is easily shown by classical phase-space arguments that their contribution to the total plasma partition function is much less than that of the adjacent continuum of free states. A similar statement holds for their contributions to the opacity (Stewart and Pyatt 1961). Thus, the equation of state can be obtained (starting from \( \alpha \) and \( kT \)) as follows: Guess \( \nu^* \) in order to get the Debye length; for each \( \nu \), compute \( K \) and (from Figure 1) \( J \); in each ionic species lower all ionization potentials by \( JkT \) and delete all ionic configurations in which the least tightly bound electron is then free; use the Boltzmann-Saha equations to find a revised \( \nu^* \), and iterate.

We are indebted to David R. Yates for his meticulous and effective execution of the numerical work.
Editor's Comments:

It was pointed out that these results are likely to be applicable only when the Onsager-Kirkwood condition is applicable, i.e., if \( y = e\phi/kT \ll 1 \) (for only then can the potential of the average force be placed equal to \( \phi \), the average potential). This however means that the results will probably be valid in Region A (where Debye theory is used) and Region B (where the effect of the ions is small) since in both these regions \( y < 1 \). By considering these two regions only, the authors are able to obtain, dependent on the number of particles in a Debye sphere, either \( e^2/D \) or \( e^2/r_o \) for the lowering of the ionization potential. Regions C and D where the Onsager-Kirkwood condition is not valid do not affect these results very much.

The Thomas-Fermi approach should be especially good in the limit of high \( Z \), since there are many free and bound electrons, and the wavelength of the electron is small relative to the distance over which the potential changes appreciably.
REFERENCES


Depression of the ionization potential, in units of the depression given by Eq. (5). Dotted line: $F = 1$. Dashed curve: Debye-Hückel model. Dot-dash curve: ion-sphere model. Solid curves: numerical integrations of full Thomas-Fermi model, for various $z^*$; the shaded areas contain the range of variation of $F$ with $\alpha$. The abscissa, $(z^* + 1)K$, is $1/3$ of the ratio (ion-sphere volume/Debye-sphere volume); $K$ is also $ze^2/DkT$, which is the Debye-Hückel depression in units of $kT$. 
VI. JUSTIFICATIONS OF THE STEWART-PYATT MODEL

B. H. Armstrong
IBM Systems Research and Development Center
Palo Alto, California

A. Physical/Intuitive Justifications

Physically, one can give a justification for a model, like the Stewart-Pyatt model, which produces the $e^2/D$ term ($D =$ Debye length) at low-density and an $e^2/r_0$ term ($r_0 =$ interparticle spacing) at high density, in the following way.

The ionization potential is the binding energy required to remove an electron from an atom. A change in this binding energy must represent a binding into the medium. At low density (and high temperature), the only such binding that is known to exist is the plasma polarization binding, the familiar $-e^2/D$ term. It would appear (physically) that there is no other first-order source of binding into the medium available until one increases the density (and lowers the temperature) until a phase change occurs. There now appears the cohesive energy by which the particles are bound into a lattice, or something like a lattice. This cohesive energy typically has a value of the order of $e^2/r_0$ where $r_0$ is the lattice, or interatomic, spacing. One would expect each of the outer, or more loosely bound, electrons to share some substantial fraction of this quantity. The physical effect of these binding energy changes can be seen by considering a gedanken experiment. Let us imagine a plasma containing atoms, ions, free electrons, and a single photon. We adjust the frequency
so that it is just able to ionize one of the originally neutral atoms.

Before the photon is absorbed we can write the total energy of the system (Plasma + Neutral atom + Photon) as \( E_p + E_0 + h\nu \), where each item is the energy of the respective system in parentheses. To an adequate approximation for the present purpose, the energy \( E_0 \) of the neutral atom can be assigned its isolated value (it does not appreciably interact with the plasma). After the photon is absorbed, the total energy of the system is \( E_p' + E_I \), where \( E_p' \) is the new energy of the plasma and \( E_I \) the energy of the ion which has been formed by the photoionization. Then we have

\[
h\nu = E_p' - E_p + E_I - E_0 .
\]

If now we include all coulomb interaction terms in \( E_p' \), we can take \( E_I - E_0 = I \).

The vacuum ionization potential of the atom. The change in \( E_p' \), i.e., \( E_p' - E_p \) will be given by \(-\frac{1}{2} \frac{Z(Z+1)e^2}{D}\), where \( Z \) is the residual ionic charge which is unity in our context, and \( D \) is the Debye length. (This is a standard result which follows directly from Equation 74.10, page 232 of Landau and Lifschitz, Statistical Physics, Addison-Wesley, Reading, Massachusetts, 1958).

We therefore arrive at (for \( Z = 1 \)):

\[
h\nu = I - \frac{1}{2} \times \frac{2e^2}{D} = I - \frac{e^2}{D}
\]

or, equivalently,

\[
\Delta I = h\nu - I = -\frac{e^2}{D} .
\]
This change in (coulomb) interaction energy is easy to obtain in the low-density limit by means of Debye-Hückel theory; the corresponding change in the high-density limit is not easily obtainable. However, from the change in cohesive energies involved, it should be $\sim e^2/r_0$ as stated previously.

B. Theoretical Justifications

H. E. DeWitt has discussed in considerable detail the statistical mechanics theory which appears to yield the result $\Delta I = e^2/D$ in the low-density and $\sim e^2/r_0$ at high density. (See Appendix A of Opacity of High-Temperature Air, Air Force Weapons Laboratory Report AFWL-TR-65-17, June 1965; also H. E. DeWitt, this conference).

It is interesting to inquire into other possible approaches which might yield more-or-less rigorous limiting values of $\Delta I$. Although I will not go into it in any detail, I would like to outline another approach which appears capable of yielding such limiting values.


First, we note that we can write $\Delta I_z \approx \frac{\partial F_c}{\partial N_z}$ where $F_c$ is the interaction correction to the free energy, $\Delta I_z$ is the I.P. lowering for an ion with charge $z$ after ionization, and $N_z$ is the number of such ions (see DeWitt, loc. cit., pp. A-7 and A-10; alternatively, we can interpret this equation as $\delta E = \frac{\partial E_c}{\partial N_z} \delta N_z$ for $\delta N_z = 1$, i.e., the change in the energy of the whole system due to making one more ion.)

Actually, this formula gives what should be the leading term. There are two more terms given by DeWitt which I will not consider, viz,
\[ \sum_{J_z} N_{J_z} \frac{\delta E_{J_z}}{\partial N_{J_z}} - \frac{2}{\beta} \left( \frac{n_0}{V} \right) b_2(\beta) \sigma_K(\Sigma_0) \]

(for notation, see the reference). The second term accounts for interactions between neutrals--
\( b_2(\beta) \) is the second virial coefficient--and should be small. The first term, which
arises from the density dependence of the electronic energy levels \( E_j \), is not necessarily
small except in the low-density limit and would have to be included for a complete
account of \( \Delta T \) at realistic densities. We do not include it here as the purpose of this
discussion is merely to call attention to another fundamental theoretical approach.

Thouless shows that the initial coulomb potential \( e_1 e_2 / r_{12} \) between two charges
\( e_1 \) and \( e_2 \) is modified by an intervening medium of number density \( \rho(r) \) in such a way
as to produce a screening between the charges. The resultant potential has the form

\[ \phi(r_{12}) = \frac{e_1 e_2}{r_{12}} e^{-r_{12}/\lambda} \]

If the particles in the medium obey classical statistics (as will be true for any particles
in the low-density, high-temperature limit), the screening length by Thouless' approach
turns out to be \( \lambda \), the Debye length.

Now the interactions which produce such a screened potential yield a contribution to
the free energy (see Landau and Lifschitz, loc. cit.) which is given by

\[ F_c = \frac{1}{2} \sum_a N_a \phi' \]

where \( a \) designates the ionic species, \( z \) the charge, \( N_a \) the number of particles of
species $a$, and where $\phi'$ is the second term in the expansion of the shielded potential:

$$\phi(r_{12}) = \frac{e_1 e_2}{r_{12}} \left( 1 - \frac{r_{12}}{\lambda} \right) - - - \text{, viz, } \phi' = \frac{e_1 e_2}{\lambda}$$

for the potential written above. We have that

$$e_1 e_2 = Z_1 Z_2 e^2, Z_1 e^2,$$

or $e^2$ according to whether particles one and two represent an ion-ion, an ion-electron, or an electron-electron pair. Thus, if we sum over all pairs we find for $F_c$:

$$F_c = \frac{1}{2} \sum_a N_a (Z_a^2 + Z_a) \frac{e^2}{\lambda}.$$

In the classical case where $\lambda$ is the Debye length we can compute \( \frac{\partial F_c}{\partial N_a} \) (from this point on we follow DeWitt, loc. cit.) to obtain

$$\Delta I \approx -\frac{e^2}{D}$$

which should be accurate in the low-density limit. If the intervening medium is a degenerate Fermi gas, the screening length turns out by Thouless' approach to be

$$\lambda = \sqrt{\frac{P_F^2}{12 \pi \rho m \rho m}}$$

where $P_F^2 = \frac{(3 \pi^2 \rho)^{2/3}}{\hbar^2}$ is the Fermi momentum, $\rho$ the mean screening-particle density, and $m$ the screening-particle mass. At high densities and low temperatures, the electrons should become degenerate Fermi particles screening the ions (or nuclei).

The screening distance given above then becomes

$$\lambda = \left[ \frac{1}{4} \left( \frac{\pi^2}{3} \right)^{1/3} a_0 \rho^{1/3} \right]^{1/2}.$$
i.e., roughly the geometric mean of $r_0$ and $a_0$. This value is smaller (usually) than $r_0$, and the above simple way of getting $\Delta I$ would yield

$$\Delta I \sim \frac{Z(Z+1) e^2}{2 \lambda}.$$

This result, at face value, is larger than if $\Delta = r_0$, the interparticle spacing, which is the result found by DeWitt.

Unfortunately, the screening potential result quoted by Thouless is only good for large $r_{12}$, so that the expansion I used is not strictly valid. The fact that the result is correct in the Debye case is more or less accidental. In the degenerate Fermi case, a more exact calculation would have to be carried out, and the term

$$\sum N_z \frac{\partial \xi}{\partial N_z}$$

involving the density-dependent level shifts included. Intuitively, one would expect the final result again to be $\Delta I \sim e^2/r_0$. 
VII. VERY DENSE PLASMAS IN THE THOMAS-FERMI STATISTICAL MODEL

by

G. LEHNER

LABORATORIO GAS IONIZZATI (EURATOM - C.N.E.N.), FRASCATI, (Italy)

ABSTRACT:

For very high pressures the degree of ionization of a plasma cannot be calculated from the Saha-equation, instead we shall use the Thomas-Fermi statistical model of the atom. This model yields the energy distribution of electrons in a self consistent potential surrounding the nucleus and one calculates the number of free electrons having sufficient energy to overcome the potential barrier at the surface of the atom. Two cases are discussed: (a) the simple Thomas-Fermi model for zero temperature, (b) its generalization to nonzero temperature.
1. **INTRODUCTION:**

In connection with experiments on the production of very high magnetic fields by explosive compression of magnetic flux contained within a hollow metallic cylinder (the so-called "liner") we became interested in the properties of very dense plasmas. Recently these experiments and some of their theoretical aspects have been discussed at a conference in Frascati (reference [1]). To summarize, one can say that magnetic fields of some $10^6$ Gauss can be obtained. The corresponding pressures are of the order of some $10^{12}$ dyn cm$^{-2}$. There is a hope that even higher fields (and pressures) can be produced in the future. Owing to Joule heating, connected with the diffusion of magnetic fields, the liner reaches temperatures of about $10^5$ oK and perhaps more. Under these conditions the originally metallic liner becomes a degenerate plasma, its density being comparable to that of solids or even larger.

It is important, therefore, to study the behaviour of such plasmas. An interesting quantity, for instance, is the electrical conductivity. It governs the diffusion of magnetic fields into the liner, one of the basic limitations to the maximum magnetic fields obtainable (references [2, 3]). As a first step one has to know the density of free electrons (degree of ionization) in such a plasma. This problem will be studied in the following report.

Although our interest in this problem was motivated by the above mentioned experiments it is of interest also in astrophysics, where dense plasmas are very important.

For low pressure plasmas, which can be considered as ideal gases,
the degree of ionization can be calculated with the help of the Saha equation, if one knows the (eventually disturbed) ionization potentials. The method can be generalized to high pressure plasmas if the chemical potentials are known together with the ionization potentials. In our case this information is not available and we have to look for another method. A rather direct method is to use the Thomas-Fermi statistical model of the atom (references [4, 5, 6]), which has been used to discuss the equation of state of very dense matter (references [7, 8, 9, 10] and further references in the survey articles [4, 5, 6]). Usually the application to the metallic state has been stressed. However, as far as the Thomas-Fermi model is concerned, there is no essential difference between a metal and a sufficiently dense plasma. The difference comes in at a later stage only, which has nothing to do with the Thomas-Fermi model. The Thomas-Fermi model gives the number of free electrons, the scattering potentials etc. If we wish to calculate the electrical conductivity, we have to make a further assumption concerning the order of structure, which can range from the complete order of a metal lattice at zero temperature to the complete or almost complete disorder of a plasma and leads to essential differences.

Perhaps it is one of the most remarkable features of the Thomas-Fermi model that it very clearly distinguishes between bound and free electrons. One considers an elementary cell containing the atom. Its volume is the specific volume per atom. As an approximation one assumes that it has the form of a sphere and that both the distribution of electrons and the electrical potential surrounding the nucleus have spherical symmetry. The potential can be calculated in a selfconsistent way from the Poisson equation. It defines the distribution of the electrons in the six-dimensional phase space. Some of the electrons have sufficient energy to overcome the electrostatic potential barrier at the surface of the atom. Their number is given by a certain
integral (over configuration space and part of momentum space) which will be given later.

For zero temperature (or sufficiently low temperatures) we use the simple Thomas-Fermi model. For higher temperatures it has to be replaced by the generalized Thomas-Fermi model as introduced by Feynman, Metropolis, and Teller (reference [9]).

As discussed in the mentioned references the Thomas-Fermi model can be applied for sufficiently high densities (pressures) only.

In the present paper we are discussing the density of free electrons. In computing it we naturally get all the other quantities characterizing the Thomas-Fermi model for the parameters chosen, the scattering potential as a function of the radius, the equation of state, the thermodynamical potentials etc. These data will be published elsewhere.

2. THE THOMAS-FERMI MODEL FOR T = 0

Let us approximate the volume per atom by a sphere of radius \( r_0 \). The electrical potential \( \psi \) and the density of electrons \( n_e \) are spherically symmetric and related by

\[
n_e(\gamma) = \frac{8 \pi}{h^3} \int_0^\infty \frac{p^2 dp}{1 + e^{\frac{p^2/2m - \gamma - \mu}{hT}}} \]

(1)
\( h \) is Planck's constant, \( k \) is Boltzmann's constant, \( T \) is the temperature, \( \mu \) is the chemical potential, \(-\mathcal{E}\) is the charge of the electron, \( m \) its mass, \( \mathcal{P} \) its momentum. For \( T = 0 \)

\[
\eta_e(r) = \frac{8\pi}{3h^3} \left[ 2m(\mu + e\varphi) \right]^{3/2}.
\]

(2)

The Poisson equation then gives

\[
\Delta \varphi = -4\pi \eta_e(r)(-e) = \frac{32\pi^2e}{3h^3} \left[ 2m(\mu + e\varphi) \right]^{3/2}.
\]

(3)

If we now define the usual dimensionless quantities

\[
\phi = \frac{r(\mu + e\varphi)}{Ze^2}, \quad \lambda = \frac{\gamma}{\alpha}
\]

(4)

where

\[
\alpha = \left( \frac{3}{32\pi^2} \right)^{2/3} \frac{\hbar^2}{2me^2Ze^2} = \frac{1}{4} \alpha_0 \left( \frac{9\pi^2}{2Z} \right)^{2/3}
\]

(5)
(Z is the atomic number and \( a_o \) Bohr's radius) we get the well known Thomas-Fermi equation

\[
\frac{d^2 \phi}{dx^2} = \phi^{3/2}\frac{1}{x^{1/2}}
\]

(6)

The appropriate boundary conditions in our case are

\[
\phi(0) = 1; \quad \phi(\infty) = \infty \phi'(\infty)
\]

(7)

where \( x_o \) is the dimensionless radius of the atom (\( x_o = r_o/\alpha_o \)). The first condition means that the potential approaches the unshielded Coulomb potential as \( r \to 0 \) and the second condition means that the atom is electrically neutral.

Calculating now the numbers of free and bound electrons per atom we find the following integrals:

\[
N_{\text{free/Z}} = 1 - J(x_o)
\]

\[
N_{\text{bound/Z}} = J(x_o) - \int_0^{x_o} \left( \frac{\phi(x)}{x} - \frac{\phi(x_o)}{x_o} \right)^{3/2} x^2 dx
\]

(8)

For \( x_o \to 0 \) we get \( J(x) \to 0 \) also, i.e. for zero radius
(infinite pressure) all electrons are free. This is a consequence of the uncertainty principle.

For an infinitely large atom, \( \kappa_0 \to \infty \), we find \( \phi(\kappa_0) \to 0 \) (i.e. the solution for which \( \kappa_0 \to \infty \) is tangent to the \( \kappa \)-axis at infinity - see the second boundary condition (7)) and \( j(\kappa) \to 1 \) as follows from equations (6) and (7). This is the case of zero pressure. All electrons are bound. The fact that we get an infinitely large atom for zero pressure shows that the model is useful for sufficiently high pressures only.

The numerical results are represented in figure 1 by the curve \( \alpha = 0 \), which describes the ionization by pressure at zero temperature. For better comparison the radius \( \kappa_0 \) of copper (\( Z = 29 \)) at normal conditions is also plotted. In that case we would find about 7 free electrons per atom. This just shows that the model is not yet reliable for normal pressure.

One could try to improve the situation by taking into account the exchange forces between the electrons, i.e. by using the so called Thomas-Fermi-Dirac model. We have done some calculations on this basis but I do not consider them as interesting. I doubt that the Thomas-Fermi-Dirac model is really consistent. Furthermore the exchange correction can be neglected anyway at sufficiently high pressures.

3. **THE GENERALIZED THOMAS-FERMI MODEL**

The simple Thomas-Fermi model is a good approximation for sufficiently small temperatures, i.e. as long as the gas of electrons is almost completely degenerate, namely if
\[ T \ll T_F = \frac{3\hbar^2}{8 m k} \left( \frac{3 n_e}{\pi} \right)^{2/3} \]  

(9)

\( n_e \) has its minimum at the surface of the atom:

\[ n_e(x_0) = \frac{8\pi}{3\hbar^2} \left( \frac{2mZe^2 q(x_0)}{\nu_0} \right)^{3/2} \]  

(10)

so that

\[ T \ll T_F = 3.5 \times 10^5 \frac{\phi(x_0)}{x_0} \frac{z^{4/3}}{1 + \exp \left( \frac{s - \eta}{1 - \eta} \right)} \]  

(11)

If this condition is not fulfilled the influence of temperature becomes important and one has to use the complete formula (1). Introducing the Fermi-Dirac integrals

\[ \bar{J}_n(\eta) = \int_0^\infty \frac{s^n ds}{1 + \exp \left( s - \eta \right)} \]  

(12)

the expression for the density can be written as

\[ n_e(r) = \frac{4\pi}{3\hbar^3} \left( \frac{2m k T}{\hbar^2} \right)^{3/2} \bar{J}_{3/2} \left( \frac{e^r + \frac{\hbar^2}{2m k T}}{\hbar T} \right) \]  

(13)
With

\[ f(y) = \gamma \cdot \frac{e^4 + \lambda^2}{kT}, \quad \gamma = \frac{r}{b} \] (14)

where

\[ b = \frac{\hbar^{3/2}}{4\pi e \left( 8\pi m^3 kT \right)^{3/4}} \] (15)

the Poisson equation gives the generalized Thomas-Fermi equation (references [9, 10])

\[ f''(y) = \gamma \int_{1/2} \left( \frac{f(y)}{y} \right) \] (16)

and the boundary conditions become (\( y_0 = r_0/b \))

\[ f'(0) = \frac{Ze^2}{b^2 kT}, \quad f(y_0) = y_0 f'(y_0). \] (17)

For the numbers of free and bound electrons we get
\[
\frac{N_{\text{free}}}{Z} = 1 - \int \left( f(\gamma), \gamma_0 \right) \\
\frac{N_{\text{bound}}}{Z} = \int \left( f(\gamma), \gamma_0 \right) = \frac{1}{f(\gamma)} \int_0^{\gamma_0} \left[ \frac{f(x) - f(\gamma_0)}{\sqrt{1 + \exp \left( \frac{f(x)}{kT} \right)}} \right] \gamma^2 \, d\gamma
\]

(18)

The integrals depend on the two parameters \( \gamma_0 \) and \( f(\gamma) \). \( \gamma_0 \) represents the radius (i.e. represents the specific volume) and \( f(\gamma) \) represents the temperature (see the first boundary condition (17)). The equations have been solved numerically for a large number of cases and the integrals \( \int (f(\gamma), \gamma_0) \) have been computed for these cases. The results are given in figure 1 (curves \( \alpha \neq 0 \)). For better comparison with the zero temperature case the results are plotted as functions of \( X_0 \). The relation between \( X_0 \) and \( \gamma_0 \) is (see equations (5) and (15))

\[
X_0 = \gamma_0 \left( \frac{2}{3} \right)^{2/3} (f(\gamma))^2/3
\]

(19)

The different curves are labeled by a parameter \( \alpha \) where due to the first boundary condition (17)

\[
\alpha = \frac{T}{Z^{1/3}} = \frac{4.65 \times 10^5}{f(\gamma)^{4/3}}
\]

(20)
Plotting curves representing the number of free electrons (figure 1) each curve decreases at first with increasing volume. Then there is transition zone around a minimum. Finally the curves increase again. The minimum is due to the competition between the classical behaviour (final increase) and quantum effects (initial decrease).

Furthermore we see that each curve approaches the curve for $\alpha = 0$ ($T = 0$) for sufficiently small radii as it has to do according to the inequality (11).

Numerical details and more data will be given elsewhere.

ACKNOWLEDGEMENTS

The authors gratefully acknowledges very interesting discussions with Dr. J.G. Linhart and Prof. N.H. March and the excellent numerical work of Dr. L. Guerri.
REFERENCES


FIGURE 1: The number of free electrons as a function of atomic radius $X_o = r_o/a$ and temperature $T$. 
\[ a = \left( \frac{3}{32 \pi^2} \right)^{2/3} \frac{h^2}{(2 m e^2 Z^{1/3})}; \quad T = \alpha \cdot Z^{4/3} \]
I. THERMAL IONIZATION EQUILIBRIUM IN HYDROGEN PLASMAS

by

H. R. Griem

University of Maryland

It has been decided that I should discuss the case of hydrogen, and
Dr. Garton more complicated systems.

I will try to discuss possible experiments that might have sufficient
accuracy to decide which correction to the Saha equation is correct.

Saha's equation may be written as

\[
\frac{N_e^2}{N_1} = \frac{(kT/\chi)^{3/2}}{8\pi^{3/2} a_0^{3}} \exp \left( - \frac{\chi - \Delta\chi}{kT} \right)
\]  

(1)

where \( N_1 \) is the ground state number density of neutral hydrogen, \( \chi \) is the
unperturbed ionization potential and \( \Delta\chi \) is the lowering of the ionization
potential which we wish to measure. It is more convenient to express the result
in terms of \( N_1 \), since then we do not have to worry about uncertainties in
the atomic partition functions, and it is also simpler to measure than the total
neutral density.

To obtain any experimental accuracy we require that \( N_e \) and \( N_1 \) be
comparable. Thus assume \( kT/\chi \approx 0.1 \) (although this may take us out of the
range of the most reliable theories). Consider now the conditions required
for a reliable measurement of \( \Delta\chi \).

Firstly, we have to measure \( N_e \) and \( N_1 \) reasonably well; let us assume
at this stage that we can measure \( N_e^2/N_1 \) to about 10%. Besides this error,
we have to consider experimental errors in temperature measurement. At the

close to the critical density and the numerical value of \( \Delta\chi \), for both the ion
The requirement that this is smaller than \( \left( \frac{\Delta N_1}{N_1} \right) \Delta T \) means that we must work at densities in excess of \( 10^{17} \text{ cm}^{-3} \).

In addition to fulfilling this criterion, we must make sure that the light source is reasonably homogeneous; so that the temperature gradients are small over the relevant mean free paths. And, in a case where there is a transient source, we must make sure that the rate of change of temperature with time is small compared to the relaxation time.

The effect that we are looking for is the change of \( N_1 \) for fixed experimentally known \( N_e \) and \( T \) which is due to the reduction of the ionization potential i.e.,

\[
\frac{\Delta N_1}{N_1} \bigg|_{\Delta X} = \frac{\Delta X}{kT} = \frac{e^2}{DkT}
\]  \( (4) \)

assuming, for further estimates, that \( \Delta X \approx e^2/D \).

If we require the error due to temperature measurement (equation (2)) to be \( \varepsilon \) times the effect; the condition on \( N_e \) for the Debye expression becomes

\[
N_e \approx \frac{1}{64\pi a_o^3} \left( \frac{\Delta T}{eT} \right)^2 \frac{kT}{\chi}
\]  \( (5) \)

\[
= 3 \times 10^{21} \left( \frac{\Delta T}{eT} \right)^2.
\]

For \( \varepsilon = 0.2 \) and \( \Delta T/T = 0.02 \), \( N_e \approx 3 \times 10^{19} \) which, although not impossible, is not very realistic, especially since at these densities a good temperature measurement would be difficult. Also, for these densities, one would be fairly close to the critical density and the numerical value of \( \Delta X \), for both the ion
sphere and Debye models would be comparable. This shows that a measurement
to 20% is just about hopeless. For larger values of $\epsilon$, the density will be
somewhat smaller, but the question now is whether the validity criteria for
LTE is more important.

If the error coming from the deviation from LTE is a factor $\delta$ of the
required effect we have the following condition on $N_e$:

$$ N_e \approx \frac{1.2 \times 10^{-7}}{a_0} \frac{kT}{\chi}^{4/3} $$

$$ = 3 \times 10^{16} \left(1/\delta\right)^{2/3} \quad , \quad (6) $$

Since $\delta$ and $\epsilon$ will be comparable quantities and we have already seen that
we must be satisfied with $\epsilon$ quite close to unity, this condition is not
critical. Thus to get any measurable effect in hydrogen we will certainly
have LTE; however, for hydrogenic ions (e.g. He$^+$) the LTE requirement would
be much more restrictive.

The conclusion is that we will probably have to put $\epsilon$ close to unity
for which $N_e \approx 1.2 \times 10^{18}$. Thus, within a factor of 2, we can, in a
hydrogen plasma of temperature about 15,000$^\circ$K and density about $10^{18}$,
determine whether, e.g., the Debye result is correct or not. However, since
we are close to the critical density, such results would not be conclusive.

Up to now we have been considering the ground state density only. If we
modify the Saha equation and measure the electron density with respect to the
density of some excited state $N_n$ (for principal quantum number $n$), the
criteria become less stringent. Experimentally also it is easier to measure
densities of excited states. Thus, the Saha equation can be written
\[
\frac{N_e^2}{N_n} = \frac{(kT/x)^{3/2}}{8\pi^{3/2}a_0^{3/2}n^2} \exp \left( -\frac{(x/n)^2 - \Delta x}{kT} \right), \quad (7)
\]

since, if we consider low-lying states for hydrogen, shifts of the energy levels will be very small and the same \( \Delta x \) will apply to all of these levels.

Now

\[
\frac{\Delta N_n}{N_n} \left|_{\Delta T} \right. \approx \left( \frac{x}{n^2kT} + \frac{3}{2} \right) \frac{\Delta T}{T}. \quad (8)
\]

For a typical excited state this error (for \( \Delta T/T \approx 0.02 \)) will be less than 4%. Since collision cross sections for excited states are larger than for the ground state, the LTE condition now for the excited state changes to

\[
\frac{\Delta N_n}{N_n} \left|_{\text{LTE}} \right. \approx \frac{10^{-7}}{N_{a_0} e_n^{1/2} n^{1/2}} \left( \frac{kT}{x} \right)^{1/2}. \quad (9)
\]

This of course does not mean complete LTE for the whole system. However the Saha equation above, (equation (7)) which assumes a Boltzmann distribution for the excited states down to principal quantum number \( n \), still allows us to measure \( \Delta x \).

In general this will not be restrictive for \( n \geq 2 \). Comparing the effect we wish to measure (for the Debye depression) with the uncertainty due to temperature errors, gives the following condition

\[
N_e = 3.3 \times 10^{22} \left( \frac{\Delta T}{eT} \right)^2 \left( \frac{x}{n^2kT} + \frac{3}{2} \right)^2 \left( \frac{kT}{x} \right)^3 \quad (10)
\]

\[
= 1.5 \times 10^{20} (\Delta T/eT)^2
\]
which for $\epsilon = 0.2$ is $N_e = 1.5 \times 10^{18}$ and $\epsilon = 1$ is $N_e = 6 \times 10^{16}$ cm$^{-3}$. At $10^{18}$ we are close to the critical density; however, if we are happy to make measurements to only a factor of 2, we could go to much lower densities where the difference between the Debye and other theories is typically a factor of 5.

The conclusion is that if we use low lying excited states, we can measure $\Delta \chi$ to sufficient accuracy to discriminate against corrections which are much larger than the Debye result. But it would be hard to fix a numerical factor in front of the Debye result.

With regard to the experimental situation, it is important to realize that all measured quantities will to some extent be affected by high density corrections (H. R. Griem, Phys. Rev. 128, 997 (1962)). For example, if we measure the electron density by measuring the optical refractivity, there will be a small uncertainty due to the contributions of electrons in highly excited states which we do not know whether to count as free or bound, and we have to make corrections. Similar problems occur for electron density measurements from the absolute continuum intensity, and correlation effects are important in Stark broadening, (e.g. for Hg). Probably the most reliable method for $N_e$ is the optical refractivity, especially since it is completely independent of temperature.

The upper state density, $N_n$, for e.g. Hg , could be derived from the absolute intensity. Since the transition probability is exactly known, the error would be that of absolute intensity measurements; say 5%. Almost certainly, $N_e^2/N_n$ can be measured to something like 10%.

The real difficulty comes in measuring the temperatures. One solution is not to work with pure hydrogen plasmas but to inject some helium and work at sufficiently high densities that even the upper state populations of He II
lines are described by LTE relations. At the densities we are considering this would be marginal and would depend to a large extent on radiation trapping; in the Saha equation for helium the effect of depression of the ionization potential on the temperature derived from comparing the intensities of lines from the neutral and ionized species would be negligible, and a 2% accuracy is just about possible.

Alternatively, in pure hydrogen, we can measure the ratio of the intensity of a line to the continuum intensity which is only a function of temperature and demands only a relative intensity measurement. The trouble here is that the lines are very broad, and it might be difficult to measure the ratio with sufficient accuracy.
II. THE PLASMA IN EQUILIBRIUM: EXPERIMENTAL ASPECTS

by

W. R. S. Garton

Imperial College of Science and Technology

London S.W.7

On considering what can be reported of an observational or experimental character embraceable under the area of interest of this Workshop, it becomes quite plain that hardly anything exists which can be called even semi-quantitative. Hence, most of this contribution will concern features of spectral transitions and series which seem of promising relevance, with some suggestions of likely useful current or projected work. In this sort of situation it is inescapable that, an otherwise undue, emphasis will be given to the interests at present engaging my own or associated laboratories.

Dr. Griem confined his remarks to the simplest atomic systems - H and He - like, -- where theory is tractable but experiments, until recently at least, have been difficult. The spectra I shall discuss involve the reverse situation, since they arise from more complex atomic structures for which theoretical development is still rather primitive, but the experiments are often fairly simple. This, of course, is the usual position in atomic physics.

There has, of course, been a great deal of experimental work of high technical and interpretive excellence during the last fifteen years or so, where problems of the sort we are interested in here, have been brought out prominently. I am here thinking of the Kiel "Water-arc" and "Cascade-arc" work, that of Olsen on convection-stabilized arcs, T-tube experiments and studies of gases heated by aerodynamic shocks. However, we leave these things aside, because while such work has served to emphasize and identify
the problems, invariably the partition-function termination and/or ionization potential depressions have been included by utilizing currently sensible-seeming theoretical models, and we know by now that these are still subject to some uncertainty.

First, I make some remarks on the tabulations of ideal ionization potentials, i.e., for isolated atomic species. These are most accurately obtained from series spectra and best of all from H-like series of large \( l \), e.g., \( ^2\!C \) series in the alkalis (Edlén). If we look at the Atomic Energy Level tables, we find large numbers of ionization potentials listed to fractions of a wave-number, but experience shows that the accuracy is usually greatly overrated. For example, some of our work at Imperial College has incidently produced long absorption series, typically to the 35th to 50th member, -- and in many cases we are able to measure unperturbed series to high accuracy, giving improved ionization potential values. Results for one such case are illustrated in Fig. 1 which shows the quantum-defect plot for the principle series of Sr I. In some cases care is needed as illustrated by Fig. 2 which shows similar plots for the In I \(^2\!S\) and \(^2\!D\) terms. It will be seen that the \(^2\!S\) series gives a Ritzian plot whereas the \(^2\!D\) series shows a marked downward curvature towards the limit. This we know to be interpretable as due to a perturbation from the \( sp^2\!D \) term which lies inside the ionization continuum. Again, the spectrum of La I, recently photographed in absorption by J. M. Wilson and myself, has revealed a previously unknown series which we identify as \( s^2d^2\!D - sp^2\!P \), the members of which show strong autoionization broadening and give a correction of about \( 315 \text{ cm}^{-1} \) to the previously accepted value for the ionization potential.

Proceeding now to the question of the depression of the ionization potential, some experiments recently done jointly with Dr. s Parkinson and Reeves at Harvard are worth mention. The experiments have been on the absorption by
the problems, invariably the partition-function termination and/or ionization potential depressions have been included by utilizing currently sensible-seeming theoretical models, and we know by now that these are still subject to some uncertainty.

First, I make some remarks on the tabulations of ideal ionization potentials, i.e., for isolated atomic species. These are most accurately obtained from series spectra and best of all from H-like series of large $L$, e.g., $^2G$ series in the alkalis (Edlén). If we look at the Atomic Energy Level tables, we find large numbers of ionization potentials listed to fractions of a wave-number, but experience shows that the accuracy is usually greatly overated. For example, some of our work at Imperial College has incidently produced long absorption series, typically to the 35th to 50th member, -- and in many cases we are able to measure unperturbed series to high accuracy, giving improved ionization potential values. Results for one such case are illustrated in Fig. 1 which shows the quantum-defect plot for the principle series of Sr I. In some cases care is needed as illustrated by Fig. 2 which shows similar plots for the In $^2S$ and $^2D$ terms. It will be seen that the $^2S$ series gives a Ritzian plot whereas the $^2D$ series shows a marked downward curvature towards the limit. This we know to be interpretable as due to a perturbation from the $sp^2$ $^2D$ term which lies inside the ionization continuum. Again, the spectum of La I, recently photographed in absorption by J. M. Wilson and myself, has revealed a previously unknown series which we identify as $s^2 d^2$ $^2D$ -- $s^2 p^2$ $^2P$, the members of which show strong autoionization broadening and give a correction of about 315 cm$^{-1}$ to the previously accepted value for the ionization potential.

Proceeding now to the question of the depression of the ionization
the plasma of shock-heated metal vapours, i.e., absorption by the plasma of shock-heated (argon plus metal) vapour; typical electron densities have been $10^{16}$ cm$^{-3}$. These reflected shocks are useful in providing a well defined column of emitting or absorbing hot gas, and we have good evidence that the plasmas are in close approximation to local thermal equilibrium. A major feature of the experimental methods developed at Harvard and independently elsewhere, has been the establishment of reliable techniques for the determination of reversal temperature, by the use of flash-tubes of the style originally developed at Imperial College. In one experiment done at Harvard the $f$-values of the Al doublet at 1932, 1936 Angstrom, due to the transition $3s^2 \, 3p \, 3p^2 \, 3s^2 \, 2s$ have been measured. Figure 3 shows the spectrum of a Ca + Al plasma obtained by introducing a mixture of Al and Ca salts into the path of the shock. We notice that the series of both Al and Ca are no longer defined in these pictures beyond about $n = 10$ to $13$, whereas on furnace spectra obtained at Imperial College we can follow the series to $n = 40$. In the determination of the $f$-values we need to use the Saha equation twice, once for Al and once for Ca, and the question of what corrections to insert for the respective ionization potentials arises. Due to our lack of confidence in the existing theoretical position we adopted a crude procedure which will probably be scorned by some of the theorists present, by terminating the two ionization potentials at the points at which the respective series vanished. No doubt this was crude but it appeared to us as good as any other guess at the time.

Some other experiments which have a bearing on our topic concern the absorption spectrum of Ba vapour near the first series limit $6s^2 1S_{1/2}$. From the work of Dr. Codling at Imperial College about 1960 we recognized some interesting intensity perturbations in the $6snp^1 1P^0$ series and the adjacent continuum, due to the presence of a doubly excited state. Specifically, the
level $5d\ 8p \ ^1P_1$ lies practically coincident with the ionization potential giving rise to a "Beutler-Fano profile", with its maximum in the continuum just beyond the limit, and its minimum amongst the converging lines of the principle series. This effect can be seen in the upper part of Fig. 4., which shows the absorption spectrum of Ba I obtained with a King Furnace and 3 metre vacuum Spectrograph. In the lower part of the same Figure is shown the absorption spectrum of the same element, produced in this case by means of a shock-heated plasma containing Ba. It will be noticed that the higher lines (above $n = 12$) are absent from the shock spectrum and two lines at 2433 and 2445 Angstrom have a decidedly different character in the two spectra. These lines are due to the same configuration $5d\ 8p$ as the Beutler-Fano resonance mentioned above but are ascribable to $^3P_1^o$ and $^3D_1^o$. As can be seen, although these two lines have the expected sharp character in the furnace Spectrum, in the shock tube spectrum the lines have broadened considerably. We interpret the effect as a "forced autoionization" of the doubly-excited levels concerned, due to the microfield depression of the ionization potential under the conditions of the shock heated plasma. We notice from the shock-tube spectra, that "level merging" does not seem to take place. Rather the impression is that the levels remain well separate but the corresponding absorption lines just die out, presumably because the contrast with the underlying continuum absorption has vanished. An obviously useful experiment, probably best done by means of the "hook method" will be to measure the relative $f$-values of the higher series lines (up to about $n = 12$ or 13) when the spectra are obtained (a) with a furnace and (b) with the shock tube. Experiments in this direction are in hand at Harvard Observatory. We notice one advantage of the technique of absorption spectra as compared with emission is that, in the former case we avoid the complication of the presence of continua extending beyond series limits of longer wavelength.
A quite recent shock-tube experiment done at Harvard has given what we believe to be the most direct check to date of the equality of the electron- and population temperatures of the plasma. In these experiments we have measured reversal temperatures on a number of normal transitions of Ca and Al, including lines involving the ground state and have obtained consistent values of population temperature. In addition we have measured reversal temperatures on the components of a red triplet of Ca I which have strongly autoionizing upper states which thus reflect the energy distribution of the electrons, i.e., the electron temperature. We find good agreement between the two sets of reversal temperatures so that the evidence for the existence of local thermodynamic equilibrium in the shocks used in our experiments is greatly strengthened. Incidentally, this experiment had the virtue of being a certain winner, since its result would either destroy a good deal of current shock-tube philosophy or, - as it did, - give direct grounds for confidence in LTE. Also, we can now use emission line strengths of strongly autoionizing transitions -- observable down to about 1600 Angstrom, -- as radiometry standards for the calibration of spectrometric equipment, with greatly increased confidence.

Interestingly, the Ca red triplet, as well as the Al 1932, 1935 doublet, occur in the solar spectrum, and detailed comparison of the line profiles in solar spectra with those in laboratory spectra has some fascination. Newsom at Harvard comparing line widths of the Ca group in the shock-tube and the sun, considers the half-widths show big differences. This result may be an indication of microfield effects in the former case, but, more probably may be explicable in terms of an electron-density gradient in the solar atmosphere.

As illustrated by the case of the Ca I red triplet, given the right light source it is easy enough to get lines involving strongly autoionizing upper states in emission, and previous pessimism on this possibility has been
exaggerated. For instance Tilford has observed lines with characteristic
'Beutler-Fano' resonance profiles in the spectrum of O III near 200 Angstrom;
in one case Tilford considers he may have found another example of "forced
autoionization". An earlier observation of emission lines from strongly
autoionizing upper states, was found by Rajaratnam and myself when we
identified a strong, and extremely diffuse, line pair near 2200 Angstrom
in the spectrum of a Cd arc in air. A rather amusing case of the same
thing is found in recent observations by Morris and Learner at Imperial College
of the spectra of a number of low pressure mercury-vapour light sources.

Mr. Morris, at that time a first year undergraduate student at this college,
noticed during the course of a laboratory experiment with a table spectrometer
that the little mercury-vapour light source he had been given produced a
diffuse line of unknown origin in the green. Investigation, in company with
his tutor Learner, showed that about 50 such lines were observable with the
same, or similar low pressure sources. Of these lines, all of which show
pronounced autoionization broadening, about half had been observed in the
distant past by spectroscopists such as Wiedemann but had not been classified
and the observations seem to have become lost in the development towards
tabulations like the Atomic Energy Level tables. The other half of the
lines are all new. Incidentally, the suspicion of Rajaratnam and myself some
years ago that we observed the $6p^2 \, 3P_2$ level of Hg I has proved justified.

Returning from these certainly related but rather indirect issues
to more direct possibilities regarding measurements of ionization potential
depression, some experiments at Argonne in collaboration with Dr. F. S. Tomkins
are worth mention. The original aim was to get the absorption spectrum of Ra I.
Owing to the undesirability of attempting to manufacture substantial charges
(of order of tens of milligrams) of Ra metal we proposed originally to use the
Nelson method of "flash pyrolysis". In this technique a finely divided solid material, placed within an absorption tube, is rapidly dissociated and evaporated by the heating produced by a flash tube wound spirally about the absorption cell. Attempts in this direction proved that absorption spectra of Ba (used a dummy material), could certainly be obtained strongly, but resembled much more closely those of the shock-tube. Moreover, we had the surprising result that during the first hundred micro-seconds after the heating flash, the Ba was almost fully ionized.

Another observation perhaps related to the question of ionization potential depression, has been made by Dr. J. M. Wilson at Imperial College. He has been studying long series spectra by means of the King Furnace and 3 metre grating and invariably finds that the length of the series observed depends on the type of background light source used for generating the continuum. Some results are reproduced in Fig. 5 which shows the In I absorption spectrum obtained with a furnace, and with flash tube and low intensity hydrogen tube as alternative background sources. We notice that the spectrum obtained with the continuously running low intensity hydrogen continuum is a good deal longer than that obtained with the flash tube. The results are typical and it is certain that we are not dealing with some effect of photographic exposure, or one due to unsteadiness of temperature or charge of material introduced. In the case of the flash tube exposures, the series seem to terminate about \( n = 40 \), but run on a good deal further when a hydrogen-tube is used to provide the background. Though the suggestion may seem far fetched, a rough calculation, - based on the Unsöld formula, - suggests that the Poynting-vector due to the flash-tube at the centre of the absorbing column is high enough to depress the ionization potential to around \( n = 40 \). Thus, we know from the work of Parkinson and Reeves at Imperial College that the flash-tubes used have (in the visible at least) brightness temperatures of order 20,000°K. In
fact, the total light emerging must be much greater than that characterizing a black body at 20,000°K, because of the large output, of light sources of this kind, in the short wavelength line spectrum. However, if we accept 20,000°K we find in typical cases that about 30 watt-cm² flux exists at a centre of the furnace used for generating the absorbing vapour. The Unsöld formula then predicts the limiting value of n to be around 40. This may be a mere coincidence, but it does appear that the intensity of the background light pulse could account for the phenomenon illustrated in Fig. 5. Of course, this interpretation may be quite wrong and the effect due to photoionization, for instance. At one time we thought it possible that the effect could be due to ionization produced by a shock-wave propagated ahead of the continuum light pulse, but this possibility has been removed in experiments where a quartz window has been inserted between flash tube and furnace.

The effects described in the last paragraph are sufficiently intriguing for us to wish to do further experiments. An obvious one is to look for the absorption spectrum in the high series line region when the absorbing vapour is simultaneously exposed to a very large light flux, e.g., from a "Nelson Spiral-Flash". When one gets down to the details of the design of an experiment of this sort, complications are pretty obvious. Another experiment, just starting at Imperial College in the hands of Dr. Pert is to look at high series lines in absorption when the absorbing vapour is placed within a tube provided with a pair of plane parallel electrodes to which a kilovolt or two can be applied.

Dr. Burgess will be explaining some ideas we have been developing towards a direct attempt at the measurement of the depression of the ionization potential, by simultaneous determination of reversal temperature and the particle densities in the Harvard shock-heated plasmas. As he will explain, the trouble at present seems to lie in obtaining accurate enough measurements, especially of T.
Editor's Comments:

It is felt that the following points from the discussion on this paper are worth mentioning:

(1) It was suggested that the use of an electric field obtained from Poyntings vector in Unsöld's formula was not the correct explanation for the observed difference in the number of lines seen in an absorption series according to the intensity of the background flash-lamp. It was thought to be due to the natural broadening of the levels, in so far as photo-absorption, photo-ionization and induced emission will considerably shorten their lifetime.

(2) The discussion indicated that the forced autoionization need not necessarily be attributed to the lowering of the ionization potential. Autoionization lines are broadened by configuration mixing with a continuum of states with the same $J$ value and parity. Such broadening therefore indicates the presence of a suitable continuum, but gives no indication of whether the perturbing levels are due to free electrons or merely merged upper members of a sequence (A. H. Gabriel).

(3) The fading out of a system of absorption lines towards high principal quantum number without visibly merging does not necessarily represent a lowering of the ionization potential. In absorption only the low angular momentum states are observed, and it was suggested that this drowning was due to mixing of levels of different angular momenta (due to, for instance, the Stark effect). This could cause a re-distribution of oscillator strength amongst previously disallowed levels (although the total oscillator strength from the level would be unaltered) and which might be sufficient to reduce the peak strength to a point where the lines are no longer detectable.
Figure 1
Figure 2
Figure 3

Absorption spectrum of shock-heated CaS + Al₂S₃
INDIUM ABSORPTION NEAR $^2P_1/2 \rightarrow ^1S_0$ LIMIT

H$_2$-TUBE

FLASH-TUBE
III. A COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

FOR THE LOWERING OF THE IONIZATION POTENTIAL IN AN EQUILIBRIUM PLASMA†

H. N. Olsen

Northrop Space Laboratories, Hawthorne, California

A novel method for determining transition probabilities from measured emission coefficients of a prominent pair of argon lines defined as reference lines (λ6965 ArI and λ4806 ArII) is presented which has been advantageously employed to judge the theoretical conclusions regarding methods to be applied in correcting the computed plasma compositions.

The emission coefficient of a spectral line emitted in watt/(cm²-sr) by a particle of number density, ni, from a volume unit at temperature, T °K, is defined as

$$S_i = A_i \left[ K_i \frac{n_i}{u_i} \exp \left(-\frac{E_{im}}{kT}\right) \right]$$  \hspace{1cm} (1)

where $K_i = 1.582 \times 10^{-4} \frac{g_m}{\lambda}$ and $g_m$ is the statistical weight of the upper energy level $E_{im}$ and $\lambda$ is the wavelength in cm. The portion of Eq. (1) in brackets is defined as the normalized emission coefficient ($S'_i$) which can be calculated directly from the plasma composition.

Figure 1 is a plot of the measured emission coefficients of the above reference lines emitted by the 1.1 atm argon plasma. This plot

---

can be represented by the following parametric equations:

\[ x = \log S_1 = \log A_1 + \log S_1^* \]
\[ y = \log S_2 = \log A_2 + \log S_2^*. \]  

If the transition probabilities are normalized to unity, a similar plot of the normalized emission coefficients is obtained as shown in Fig. 1 where the results of three different methods for correcting the composition for the lowering of the ionization potential are shown.

The results of the theoretical discussions during this workshop session might be summarized in the following way:

\[ \Delta \chi = \alpha_m \frac{e^2}{r_o} + \alpha_p \frac{e^2}{D} \]  

where \( r_o = \left( \frac{3}{4\pi n_i} \right)^{1/3} \) and the coefficients cannot be determined to better than an order of magnitude. The question remains as to whether, at electron densities below the critical density, the \( e^2/r_o \) term should be retained. Up to the present time it has been generally concluded that the \( e^2/D \) term is all that should be retained. A review of plasma composition calculations made using four different forms of Eq. (3) has shown the following range of numerical values for the coefficients \( \alpha_m, \alpha_p, \) and for \( \Delta \chi \) under the conditions: \( T = 16,000^\circ K, \ n_e = 2 \times 10^{17} \) and \( n_e \approx 10^{20}. \)

<table>
<thead>
<tr>
<th>Author</th>
<th>( \alpha_m )</th>
<th>( \alpha_p )</th>
<th>( \Delta \chi ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye-Hückel</td>
<td>0</td>
<td>1.0</td>
<td>0.09</td>
</tr>
<tr>
<td>Unsöld</td>
<td>3.0</td>
<td>0</td>
<td>0.44</td>
</tr>
<tr>
<td>Ecker-Weizel</td>
<td>2.9</td>
<td>0.8</td>
<td>0.52</td>
</tr>
<tr>
<td>Brunner</td>
<td>5.2</td>
<td>0.8</td>
<td>0.85</td>
</tr>
</tbody>
</table>
It is, perhaps, significant to note that the value for $\Delta\chi$ determined from the measured shift$^1$ of the series limit of the electron continuum for recombination into the lower 3s state of the atom is 0.84 ev. Until recently it has been considered$^2$ wrong to associate the $\Delta\chi_r$ measured from radiation measurements with the $\Delta\chi_s$ to be used in the Saha equation. In the light of the previous theoretical discussions there seem now to be less positive reasons for differentiating between the two values. The agreement of $\Delta\chi_s$ and $\Delta\chi_r$ in the Brunner case may turn out to be more than fortuitous.

The experimental points plotted in Fig. 1 represent averages of at least six independent measurements. By "independent" is meant that intensities of the two lines were measured at the same position in a given arc but that each set of measurements was made in a different arc in the sense that it had been restructured with replaced electrodes at the same current and pressure. Measurements in the same arc were also made at three different positions along the arc axis; the points at the top of the curve were measured near the cathode and those at the bottom midway between the electrodes. The deviation of experimental points toward lower values for the $\lambda 6965$ ArI line at the lower temperature has been explained$^3$ by absorption of the cooler layers of gas through which one must look to observe the core of the plasma.

The comparison of theoretical and experimental results in Fig. 1 shows that it would probably be difficult, even with an accurate correction for self-absorption, to differentiate with confidence between the three theories purely on the basis of the shapes of the curves. This is due to the fact that the differences of the theoretical curves when
normalized to the ion line maximum are of the same magnitude as the experimental errors which, in Fig. 1, are about ±5%.

A far more sensitive criteria for determining the numerical constants in Eq. (3) is the distances the normalized curves must be translated to fit the experimental data. These shifts, as pointed out above, are just the transition probabilities which are compared in Table II below with the best available theoretical and independently measured experimental values.

<table>
<thead>
<tr>
<th>Author</th>
<th>$A_{6965} (x 10^7)$</th>
<th>$A_{4806} (x 10^7)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye-Hückel⁴</td>
<td>0.53</td>
<td>7.86</td>
</tr>
<tr>
<td>Ecker-Weizel⁵</td>
<td>0.67</td>
<td>9.20</td>
</tr>
<tr>
<td>Brunner⁵</td>
<td>0.82</td>
<td>10.7</td>
</tr>
<tr>
<td>Thorne-Chamberlin⁶</td>
<td>0.87</td>
<td>--</td>
</tr>
<tr>
<td>Garstang (Th.)⁷</td>
<td>0.89</td>
<td>7.88</td>
</tr>
</tbody>
</table>

Unfortunately the results are not definitive in that a comparison with the theory leads to either the Debye-Hückel or Brunner form depending on whether the ion (4806) or the atom (6965) line is used. Based on the results of Table II alone, one could select the Brunner form on the basis that the experimental values for $A_{6965}$ agree well with both the theoretical and independently measured experimental value of Thorne and Chamberlin⁸. This conclusion is further supported by a comparison of ion line transition probabilities independently determined by Bennett, et al⁸, from measured relaxation of ionic lines in the output of an argon laser. Since the 4806 line was not included, a direct comparison could not be
made with the results of Table II. The transition probabilities of four other ion lines could be compared with the experimental values determined in the manner outlined above. These results are given in Table III below.

<table>
<thead>
<tr>
<th>Ion Line</th>
<th>Bennett, et al</th>
<th>Debye-Hückel</th>
<th>Olsen</th>
<th>Ecker-Weizel</th>
<th>Brunner</th>
<th>Garstang Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 4579</td>
<td>11.4</td>
<td>7.44</td>
<td>8.82</td>
<td>10.4</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>A 4658</td>
<td>11.5</td>
<td>6.95</td>
<td>8.21</td>
<td>9.70</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>A 4765</td>
<td>10.6</td>
<td>5.40</td>
<td>6.38</td>
<td>7.58</td>
<td>7.09</td>
<td></td>
</tr>
<tr>
<td>A 4806</td>
<td>--</td>
<td>7.86</td>
<td>9.20</td>
<td>10.9</td>
<td>7.88</td>
<td></td>
</tr>
<tr>
<td>A 4880</td>
<td>11.0</td>
<td>6.59</td>
<td>7.77</td>
<td>9.19</td>
<td>7.71</td>
<td></td>
</tr>
</tbody>
</table>

The consistently lower theoretical values of Garstang and the tendency of the experimental values of Olsen determined with the Brunner form of Eq. (3) toward agreement with the laser values of Bennett, et al, are convincing indications but not sufficient evidence in themselves for concluding that both terms of Eq. (3) should be retained. Coupled, however, with the results of the comparison of A6965 atomic lines above, they represent the most convincing experimental evidence in support of the theory of Ecker and Kröll which claims that the e²/r₀ term must be retained below the critical electron density. Before any conclusion can be reached it is essential that improved theoretical values for the ion transition probabilities be computed. It is the author's hope that this discussion will stimulate further theoretical and experimental work in this direction.
Editor's Comments:

It was remarked that Griem's Criteria (Plasma Spectroscopy: McGraw-Hill (1964)) for an inhomogeneous plasma had been used to show that this arc is in local thermodynamic equilibrium.
REFERENCES


\( \lambda6965 \text{ Ar I emission coefficient (} S_1 \text{ or } S_2^* \text{)} \)

**Fig. 1**
IV. A PROPOSED EXPERIMENT TO STUDY THE DEPRESSION  
OF THE IONIZATION POTENTIAL IN A PLASMA

D. D. Burgess  
Physics Department, Imperial College  
London, U.K.

W. H. Parkinson  
Harvard College Observatory  
Cambridge, Mass.

E. M. Reeves  
Harvard College Observatory  
Cambridge, Mass.

(Paper presented at conference by D. D. Burgess)

The title of this contribution did not appear in the original Conference  
programme as no start has yet been made on the experimental work. However, an  
outline of the proposed experiment may be of some interest in view of Professor  
Griem's paper, as it seems possible to avoid some of the difficulties he  
mentioned.

Conclusions essentially similar to those of Griem were reached at  
Imperial College during the course of diagnostic work on discharges with  
densities and temperatures much the same as those of the plasma produced in a  
T-tube. Indeed, the T-tube developed by Griem and his co-workers seems  
the most suitable source for experiments on the depression of the ionization  
potential produced by plasmas with temperatures in the range 15,000°K to
20,000°K. However, there are certain fundamental difficulties where one aims to substitute absolute values into Saha's equation, as proposed by Griem. The diagnostic techniques employed must be as free as possible of all systematic errors, and in particular the atomic parameters assumed must be known to an unusually high degree of accuracy.

The type of pressure driven shock tube exploited at Harvard College Observatory produces a plasma with parameters rather different from the plasma produced in T-tube. The Harvard shock tubes have several advantages in experiments aimed at measurement of ionization potential depressions. For instance, the parameters of the plasma produced make possible the use of diagnostic techniques of high accuracy. However, the most important advantage is that it should be possible to vary the electron density in the plasma over a wide range whilst keeping the temperature relatively constant.

These shock tubes work under cold burst conditions, the shock wave being driven into pure argon, and observations being made on the plasma produced by reflecting the shock at the end of the tube. The temperature in the region of the reflected shock can be varied between 4,000°K and 7,000°K by altering the burst conditions; argon is negligibly ionized in this range. The free electron population is produced by the ionization of low ionization potential metals, deliberately added impurities. Typically at 5,000°K the neutral argon density would be of the order of $7 \times 10^{18}$ atoms cm$^{-3}$ and 1 part in $10^3$ of added Calcium would give an electron density of about $5 \times 10^{15}$ cm$^{-3}$.

The proposal is to use Caesium as the dominant impurity, and by varying the amounts added to vary the electron density over as wide a range as possible, hopefully between $5 \times 10^{15}$ cm$^{-3}$ and $10^{17}$ cm$^{-3}$. Because of the low ionization potential and hence high percentage ionization of the Caesium the higher of these densities represents an impurity concentration of only 5%. The
temperature is largely controlled by the high neutral argon density, and should not be too greatly altered by this level of impurity concentration. Adjustment of temperature can, in any case, be made by varying the burst conditions. For reasons that will become apparent below, the Caesium ionization will not itself be studied. Instead, it is intended to add a small percentage of Calcium and to make an attempt to measure directly the temperature, $T$, electron density $n_e$ and the neutral and ionized Calcium particle densities $n_0$ and $n_+\,\text{,}$ and so to study the appropriate Saha equation.

This procedure has two important advantages. Firstly, it permits the use of diagnostic techniques of very high accuracy. Secondly, varying the electron density should eliminate all systematic errors in the diagnostics from the analysis of the results.

The relatively low temperature allows the use of the reversal technique of temperature measurement and such measurements on shock tubes have given results which are believed to be accurate to within $\pm 2\%$. A large part of this error is due to uncertainties in the optical path etc., which are systematic and are of no consequence in the present experiment. In addition the technique of making such measurements on lines with autoionizing upper states, which has already been mentioned by Professor Garton, allows a sensitive test to be made of the validity of the Local Thermodynamic Equilibrium assumption. It should in fact be possible to put experimentally determined limits on the accuracy within which Saha's equation is valid.

The neutral and ionized Calcium particle densities can be measured by an application of the Roschdestvensky 'hook' technique, using a Mach Zehnder interferometer, the short duration background source used providing the time resolution. This technique could not be used with Caesium since the resonance lines of CsII lie in the Vacuum ultraviolet.
It is intended to monitor the electron density by observing a Stark-broadened line of Caesium, using a rapid scanning Fabry Perot. This instrument has an ultimate time resolution of better than 1 microsecond, in which a complete line profile can be recorded, very much shorter than lines in which the plasma changes appreciably. The Stark broadening parameters for Caesium calculated by Griem have been checked experimentally by Agnew and Stone, but in any case in the present experiment the absolute accuracy is irrelevant. All that is of interest is the proportionality between the line width and the electron density, which is one of the most firmly established parts of all line broadening theories.

One would like to measure the electron density interferometrically, but both Mach-Zehnder and He-Ne Laser techniques are useless in the visible region of the spectrum because of the large contribution of the neutral argon to the refractive index in this wavelength range. The recently developed CO₂ laser operating at a wavelength of 10 microns might be one solution to this problem, although its use is not contemplated at present.

It will be noticed that these diagnostics form a very nearly 'diagonal matrix' - that is the various measurements are based on physical principles which are completely independent of one another. For instance, they do not depend on the theoretical cancellation of one parameter in the ratio of two observables used to measure another. This seems an important property in experiments of this type, and would give one more confidence in the physical meaning of any results which might be obtained. In the diagnostics described above the only 'off-diagonal' effect is the very weak dependence of the line broadening parameters on the temperature.

By making observations at various electron densities one can essentially study the logarithm of Saha's equation. This procedure eliminates any systematic errors in the measurements from the analysis - it is no longer the absolute
value of $\frac{n_+ n_e}{n_o}$ which matters, but the variation of this quantity with $n_e$.

Thus errors in the oscillator strengths used in the 'hook' determinations of $n_+$ and $n_o$ are irrelevant, producing as they do a constant error in $\frac{n_+}{n_o}$. Similarly the absolute value of the broadening parameter used in the determination of $n_e$ is unimportant. In experiments designed to study the depression of the ionization potential by measurement of the absolute value of $\frac{n_+ n_e}{n_o}$ the most important error is that in the temperature, particularly because of the small size of the depression in comparison with the ionization potential itself. In the experiment proposed here again only random errors matter, systematic errors merely altering the effective ionization potential by a constant amount.

A second advantage of this type of technique is that it distinguishes in principle between the physical mechanisms producing the depression. In the case of a direct experiment the results could be fitted to either theory by appropriate adjustments of the constants in front of the theoretical expressions for the depression. In the present case the constants determine whether the effects of the depression are large enough to be measurable, but it is the functional variation of the depression as the electron density is varied that is studied.

The remaining question is whether the random errors can be sufficiently reduced for meaningful results to be obtained. The lowest electron density at which it is worth making observations is that at which the smaller of the 2 possible depressions (the Debye value) alters $\frac{n_+ n_e}{n_o}$ by an amount equal to the random errors in measuring this quantity. If these errors are assumed to be of the order of 5% the lowest worthwhile density, assuming a temperature of 5,000°K,
is about $5 \times 10^{15}$ electrons cm$^{-3}$. At this temperature the critical density is rather larger than $10^{17}$ electrons cm$^{-3}$, and over the range between $5 \times 10^{15}$ cm$^{-3}$ and $10^{17}$ cm$^{-3}$ the difference in the changes of the depression predicted by the Debye and the Ecker-Kröll theories corresponds to a difference in $n_{+} + n_{e}$ of somewhat greater than 5%. Consequently, by taking readings at a large number of electron densities and the curve fitting, it should be possible to distinguish between the two theories. Indeed a distinction between the Debye theory and the original Unsöld value could be made on the basis of measurements at only two densities.

Significant changes in the value of the depression predicted by the Debye theory could also be produced by varying the temperature over the experimentally possible range. The depression predicted on the $e^{2}/r_{o}$ theory is, of course, independent of temperature. By appropriate analysis this technique could also produce results which were at least statistically in favor of one or other theory.

One remaining problem is to estimate what effect the high neutral argon density would have on the depression. However as this density can be kept fairly constant, provided its effect is not dominant, the other mechanism, could still be studied.

In conclusion, this approach, like Griem's, relies on making observations of effects which are not much greater than experimental errors. However, in contrast to Griem's proposed experiment, ours has the advantage that the only errors of consequence are purely random, and hence at least in principle could be reduced to within arbitrarily small limits. Certainly a statistical analysis of a large number of runs would be needed, but if the temperature were varied as well as the electron density and the results were analyzed in an appropriate way there would seem to be some hope of obtaining experimental results of significance.
REFERENCES

[NOTE: These references have been added by the editor and are therefore not necessarily the same as those the authors would have chosen]

1. W. R. S. Garton: This conference.
V. PROPOSAL FOR AN INVESTIGATION OF HIGHLY EXCITED STATES IN A DISCHARGE BY MEANS OF A TUNABLE LASER BEAM

by

B. Brehm

Joint Institute for Laboratory Astrophysics

Highly excited states of atoms are very sensitive to perturbation by external fields or charged particles in a discharge. A measurement of the shift and broadening of such states can be used to investigate these perturbations. The difficulties of high resolution absorption measurements in a discharge can be overcome with the help of a tunable laser beam. This technique has been used by H. J. Gerritsen and M. E. Heller to measure the absorption due to vibrational excitation of molecules.

Unfortunately the energy range over which a laser can be tuned is very small. Of the three possibilities A) thermal shift, B) magnetic shift, C) modulation by ultrasonic waves or microwaves B) and C) have the advantage that they may be calibrated. Modulation by microwaves seems the most promising approach.

The limited size of the tuning range makes it necessary, to match the laser transition to the discharge material. Assuming that a shift of $10^{-4}$ eV can be accomplished, the published gas laser lines have been compared with atomic transitions. The following cases are promising. (All wavelengths in air.)

I. Cesium (ground state) $^{2}S_{1/2} \rightarrow ^{2}P$ 3191 50 Å $= 31324$ 11 cm$^{-1}$

   laser: chlorine $^{4}S_{1} \rightarrow ^{4}P_{2}$ 3191 43 Å $= 31324$ 86 cm$^{-1}$

   $\Delta E = 0.75$ cm$^{-1}$
Using the Rydberg formula one can easily show that at least one highly excited state lies within the tuning range of $10^{-4}$ eV whenever the laser line excites an atom to a state with an effective quantum number $n^* > 65$. This is equivalent to the requirement that the state to be excited by the laser line must be closer to the ionization limit than $6.4 \times 10^{-3}$ eV $\approx 51 \text{ cm}^{-1}$. This criterion and the fact that the metastable states mentioned below may be expected to be highly populated in any discharge lead to the conclusion that the following atoms can also be used for this experiment.

II. Barium (metastable) $6s^2(2S)5d^2D \rightarrow \text{limit } 3046.31 \AA = 32816.9 \text{ cm}^{-1}$

laser: argon II

3047.03 \AA = 32809.1 \text{ cm}^{-1}

$n^* \approx 120$

A shift of only 0.13 cm$^{-1}$ is necessary in this case.

III. Helium (metastable) $2s^1S_0 \rightarrow \text{limit } 3120.86 \AA = 32033.27 \text{ cm}^{-1}$

laser: Fluorine III $3p^4D_{7/2} \rightarrow 3s^4P_{5/2} 3121.56 \AA = 32026.0 \text{ cm}^{-1}$

$n^* \approx 120$

The necessary shift is 0.12 cm$^{-1}$. Using He$^3$ the distance to the ionization limit reduces from 7.3 cm$^{-1}$ to about 5 cm$^{-1}$ or the effective quantum number of the excited state increases to 140. The necessary shift for He$^3$ is only about 0.08 cm$^{-1}$.

It can be expected that new laser lines will increase the number of atoms which can be excited to states close to their ionization limit. Of the three cases listed above especially the two later ones promise interesting results on the influence of fields on highly excited states of atoms.
REFERENCES

SUMMARY OF DISCUSSIONS

Much of the discussion of this conference was concerned with how one defines a free or bound particle. This definition is ambiguous, in so far as there must be a transition region where particles can be considered as neither completely free nor completely bound.

The usual definition is from an energetic viewpoint and treats as free those electrons and ions in the plasma for which the pair energy with the nearest oppositely charged neighbor is positive. This means that a free electron has sufficient energy to escape from the ions within the plasma.

Within this conventional definition (Dr. Ecker's so called 'naive' definition) there was fairly general agreement. The lowering of the ionization potential in Saha's equation and the cut-off of the summation for the atomic partition function should be at the same energy: \(- e^2/D\) below the critical density and \(- e^2/r_o\) above the critical density. (The critical density is that density at which there is one particle within a Debye sphere; \(D\) is the Debye-length and \(r_o\) is the mean interparticle distance). The Coulomb interactions between the free particles are taken into account by this cut-off at the free-bound limit; further interactions are neglected and unperturbed values of the energy levels are used up to this limit. This is obviously an approximation, however, observations which can be made up to the Inglis-Teller limit, where individual lines are no longer distinguishable, reveal only small line shifts. No observations can be made between the Inglis-Teller limit and the cut-off.
Ecker and Kröll define their free and bound particles in terms of the localizability of the wavefunctions — a bound particle is one in which the smallest average quantum-mechanical distance to the nearest oppositely charged neighbor (roughly the extent of the wavefunction) is much less than the mean interparticle distance, similarly the particle is considered free when these distances become comparable. In a stationary solution of the problem these average distances are clearly defined.

Thus, within this picture, the electrons whose wavefunctions overlap a few ions are no longer related to a single ion and should be capable of moving on equipotential surfaces through the plasma, and could contribute to some extent to, for instance, the mobility. Ecker and Kröll realize that there is always an approximation in treating particles in terms of weak or strong pair correlations, as either completely free or completely free or completely bound. There is always a transition region where particles are influenced by higher order correlations and quantum-mechanical effects. Much of the discussion concerned this transition region where the Physics of the problem is unknown. However there is no satisfactory theory for the kinetics of particles with quantum-mechanical multiple correlations. Within the pair correlation model a discontinuous junction between free and bound is inevitable. Ecker and Kröll claim that the subdivision in free and bound particles derived from their quantum-mechanical calculations is more appropriate than the conventional one.

There was a certain amount of discussion which indicated that electrons which might be 'free' for one phenomenon (e.g., mobility) might not necessarily be 'free' for another (e.g., to contribute to refractive index or
even the hydrostatic pressure). It should be possible to write a consistent Saha equation for the composition of the plasma, and treat as 'high density corrections' the differing number of electrons contributing to the various phenomena, rather than a separate Saha equation for each phenomenon. In this way the correct observable for the physical effect can be produced.

Accounting for the free-bound interaction, Ecker and Kröll derive from their analysis (for below the critical density), that the maximum energy of bound states is \(-\frac{e^2}{r_0} + \frac{e^2}{D}\). All electrons with energies greater than this are considered free, so that the lowering of the ionization potential (above which the particles are free) is \(\Delta \chi \sim \frac{e^2}{r_0} + \frac{e^2}{D}\) where the \(\frac{e^2}{D}\) term comes, as usual, from the interaction of the charged particles in the Debye approximation and the \(\frac{e^2}{r_0}\) term comes from the free-bound interaction reflected in their new definition of free and bound.

In detail, the equilibrium of the system is found by minimizing the free-energy. It was stated that the total free energy of the system (which includes an additive term due to the interaction between the particles in the Debye approximation) is the same no matter which definition of free and bound is taken. However, the total partition function is split into a product describing free and bound separately, and Ecker and Kröll do this in a different manner (thus some particles are free by their definition which would not be free by the conventional definition). It is this difference in subdivision that causes a change in representation of Saha's equation. This procedure will be consistent provided, as was claimed, that a zero of energy which does not depend on the number of particles is used. It is reasonable to suppose that different definitions get different
answers, although the total number of particles is constant no matter how
they are counted.

During the conference Ecker and Kröll claimed that the lowering of
the ionization potential to be used in the Saha equation should be
\[
\Delta \chi_s = \eta \frac{e^2}{r_o} + \frac{e^2}{D}
\]
where \(\eta \sim 1\) was admitted to be an uncertain
quantity due to the uncertainty arising from the free-bound interaction.
Since the conference Ecker and Kröll have elaborated on the calculation
of \(\eta\) and by interpolating the partition function through the
"quasi-free" region have found the value
\[
\eta \sim 0.7 \left(\frac{r_w}{r_o}\right)^{1/2} = 0.4 \frac{r_o}{D}.
\]
It follows that the contribution of the free-bound interaction to \(\Delta \chi_s\) is
0.4 \(\frac{e^2}{D}\) which is still very much larger than the higher order contributions
from the free-free interaction. The Saha equation for the number of
electrons and ions (within their definition) thus has a value of
\[
\Delta \chi_s = 1.4 \frac{e^2}{D}.
\]
It should also be noticed that \(\Delta \chi_s\) is not equal to \(\Delta \chi\)
(the maximum energy of the bound states).

It remains to be seen how sensitive the number of free electrons is
to the definition of just what is free and bound -- this will now mean
a comparison between the atomic partition function cut-off at \(-\frac{e^2}{D}\), and
the partition function cut-off at \(-\frac{e^2}{r_o}\) and multiplied by the factor
\(\exp\left(-0.4 \frac{e^2}{D}\right)\).

There was some feeling at the conference that the results should be
moderately insensitive to where the division is made, provided that the
\(-\frac{e^2}{D}\) term due to the interaction is included. This seems to imply that
the number of occupied states in the transition region is likely to be
small.
During the conference there was general agreement that the bound states could approximately be described in terms of hydrogenic eigenfunctions up to an energy \( E_h \approx -\frac{e^2}{r_o} \left( \frac{r_o}{a_o} \right)^{1/5} = E_{h(IT)} \) where \( a_o \) is the Bohr-radius. This is the Inglis-Teller value where levels, due to their broadening, merge into the continuum. This limit is obtained in answer to the question of how the interaction of the free particles effects the eigenfunctions at the atom, which is to be separated from the question when is the particle free and bound. Ecker and Kröll state in their manuscript that the inclusion of nonstatic effects causes a deviation from the Inglis-Teller formula, resulting in the limit

\[
E_h = E_{h(IT)} \left( \frac{r_o}{D} \right)^{1/2}.
\]

There was also general agreement amongst the speakers (see in particular Jackson and Klein) that shifts of the ground state energy of a neutral atom of the order of \(-\frac{e^2}{D}\) are spurious, and any energy shift due to polarization of the neutral atom in the plasma will be zero to first order (and definitely much less than \(-\frac{e^2}{D}\)).

One further approach to the problem of the lowering of the ionization potential was raised during the discussion, although it was not argued in detail. This implied that states of large principal quantum do not exist when the ionization frequency (due to electron collisions) is so high the the lifetime of a given state is less than one Bohr period for that state. The electron cannot then be attributed to a single state and has to be treated as continuous. It was claimed that this gave a contribution (to be added to \(-\frac{e^2}{D}\)) comparable to \(-\frac{e^2}{r_o}\).
With regard to experimental verification, these will have to be done at sufficiently high density for local thermodynamic equilibrium to be valid. For hydrogen, Griem concludes that, given the present precision in determining the relevant plasma parameters, measurements using low excited states could probably be made to determine the Debye correction to within a factor of about two, which, at the densities considered, would be sufficient to discriminate against corrections as large as \(-\frac{e^2}{r_o}\).

The method proposed by Burgess and his colleagues would be more convincing in so far as they are not looking for the actual lowering of the ionization potential, but rather its functional variation with electron density, \(n_e\). Most of the systematic errors in their experiment should cancel out, and it should be possible to make the random errors sufficiently small to tell whether the lowering in Saha (\(\Delta\chi_s\)) is proportional to \(n_e^{1/2}\) (from \(\frac{e^2}{D}\)) or \(n_e^{1/3}\) (from \(\frac{e^2}{r_o}\)). This result will depend on the physics of the interaction, and in this case a constant multiplying factor for \(\frac{e^2}{D}\) or \(\frac{e^2}{r_o}\) cannot be used to fit the results, as could happen in the case of a single spot determination.

It would appear however that the method of Olsen could give the most sensitive test of \(\Delta\chi_s\). Here measurements are made of the emission coefficients of both neutral and ion lines of the same species which are emitted from a constant pressure arc plasma which according to the usual criteria is in local thermodynamic equilibrium. To relate these emission coefficients to the oscillator strengths of the lines it is necessary to determine the populations of the states, giving rise to the lines, by a composition calculation using Saha's equation. It turns out that the oscillator strengths derived
in this way are very sensitive to the $\Delta \chi_s$ used (20 - 30% variations being quite possible), so if alternative accurate values of the oscillator strengths are available, this could determine the correct value of $\Delta \chi_s$. The experimental evidence is as yet by no means conclusive, but Olsen's results indicate that, in contrast to the weight of theoretical opinion, a term in $e^2/r_0$ should be retained in $\Delta \chi_s$ below the critical density.*

*Precise determinations of some Ar I and II transition probabilities using a wall-stabilized arc have recently been published by C. H. Popenoe and J. B. Shumaker (J. Res. Natl. Bur. Std. 69A, 495 (1965)). According to W. L. Wiese (Private Communication) a much better agreement between these results and some new lifetime determinations by J. Klose is obtained by using the Debye radius in the lowering (rather than the interparticle distance).
ARMSTRONG, B. H.
Space Research & Development Center
I.B.M.
2670 Hanover Street
Palo Alto, California

BRANSCOMB, L. M.
J. I. L. A.
University of Colorado
Boulder, Colorado 80302

BREHM, B.
Research Associate, J.I.L.A.
University of Colorado
Boulder, Colorado 80302

(After 1 September 1966:
Physikalisches Institut der
Universitat Freiburg
(78) Freiburg i. Br.,
Hermann-Herder Str. 3, Germany)

BRITTIN, W.
Chairman, Department of Physics and
Astro. & J.I.L.A.
University of Colorado
Boulder, Colorado 80302

BURGESS, D. D.
Physics Department
Imperial College
London S.W. 7
England

COOPER, J.
J. I. L. A.
University of Colorado
Boulder, Colorado 80302

COX, J.
J. I. L. A.
University of Colorado
Boulder, Colorado 80302

DeWITT, H. E.
Lawrence Radiation Laboratory
P. O. Box 808
Livermore, California

DRAWIN, H. W.
Groupe de Recherches de l'Association
Euratom-CEA sur la Fusion
Boîte Postale No. 6
Fontenay-aux-Roses (Seine)
France

ECKER, G.
Institut fur Theor. Physik
Universitat Bochum
Wegelerstrasse 10
Germany

FERGUSON, E.
National Bureau of Standards
Boulder, Colorado 80302

GABRIEL, A. H.
U. K. A. E. A.
Culham Laboratory
Culham, Abingdon, Berkshire
England

GARTON, W. R. S.
Physics Department
Imperial College
London, S. W. 7
England

GELTMAN, S.
J. I. L. A.
University of Colorado
Boulder, Colorado 80302

GILMORE, F.
Rand Corporation
Santa Monica, California

GRIEM, H. R.
Department of Physics and Astronomy
University of Maryland
College Park, Maryland

vON HAGENOW, K. U.
Institut fur PlasmaPhysik
8046 Garching bei
Munich, Germany
Participants
Page 2

HOCHSTIM, A.
I.D.A.
400 Army-Navy Drive
Arlington, Virginia

HUNGER, K.
Visiting Fellow, J.I.L.A.
University of Colorado
Boulder, Colorado 80302

(After 1 September 1966:
Institut fur Theoretische Physik
Technische Hochschule
Hanover, Germany)

JACKSON, J.
Howard University
Washington, D. C. 20001

KLEIN, L.
Howard University
Washington, D. C. 20001

KRÖLL, W.
Institut fur Theor. Physik
Universitat Bochum
Wegelerstrasse 10
Germany

LANE, N. F.
Visiting Fellow, J.I.L.A.
University of Colorado
Boulder, Colorado 80302

(After 1 September 1966:
Rice University
Houston, Texas 77001)

LEHNER, G.
Laboratorio Gas Ionizzati
Euratom - CNEN
Frascati, Roma
Italy

McLANE, K.
National Bureau of Standards
Boulder, Colorado 80302

OLSEN, H. N.
Northrup Corp.
P. O. Box 1525
Los Angeles, California

PARKINSON, W.
Harvard College Observatory
Cambridge, Massachusetts 02138

PERSSON, K. B.
National Bureau of Standards
Boulder, Colorado 80302

REEVES, E.
Harvard College Observatory
Cambridge, Massachusetts 02138

SCHLUTER, H.
Department of Physics
University of Texas
Austin, Texas 78712

SHUMAKER, J.
National Bureau of Standards
Boulder, Colorado 80302

STEWART, J. C.
Visiting Fellow, J.I.L.A.
University of Colorado
Boulder, Colorado 80302

(After 1 September 1966:
General Atomic
Division of General Dynamics Corp.
P. O. Box 608
San Diego, California 92112)

WEINSTOCK, J.
National Bureau of Standards
Boulder, Colorado 80302

WIESE, W. L.
National Bureau of Standards
Washington, D. C. 20234
APPENDIX
BIBLIOGRAPHY OF RESEARCH ON
LOWERING OF IONIZATION POTENTIALS IN PLASMAS*

S. G. Brush
Harvard Project Physics
Harvard University
Cambridge, Massachusetts

and

B. H. Armstrong
Systems Research and Development Center
IBM Corporation
Palo Alto, California

*Part of this work was performed while the authors were associated with
Lockheed Research Laboratories, Palo Alto, California.
We give herein a brief bibliography of theory and experiment regarding the effect of interactions with other particles on the ionization potential of an atom. In order to understand the point of view from which this subject is being considered we should mention two things. First, we are not reviewing the papers cited, except to give a brief comment on their content, or supposed content. Second, the quantity of concern to us in compiling this bibliography was the "mean opacity" of a plasma, which is some kind of average of the absorption coefficient of the system for radiation of frequency $\nu$, viz. $\mu_\nu$. Ordinarily, this absorption coefficient is calculated on the assumption that radiation is absorbed independently by single gas molecules. Hence if the number density of particles of type $s$ in state $J$ is denoted by $N_{sJ}$ and the cross-section for absorption of a photon of frequency $\nu$ by a particle of type $s$, in a transition which carries the particle from the state $J$ to the state $J'$ be denoted by $\sigma_{sJJ'}(\nu)$, then the absorption coefficient $\mu_\nu$ is given by

$$\mu_\nu = \sum_{s,J,J'} N_{sJ} \sigma_{sJJ'}(\nu). \tag{1}$$

It is assumed, in doing this kind of calculation, that the problem can be separated into two independent parts: (1) the calculation of the "occupation numbers" $N_{sJ}$; (2) the calculation of the absorption cross sections $\sigma_{sJJ'}(\nu)$. This assumption is certainly correct in the low density limit, where the interactions between particles can be neglected. In that case, one may compute the occupation numbers from the Saha equation, using the experimentally observed ionization potentials. (It will be assumed that we are dealing only with atoms, ions, and electrons, and that the temperature is high enough that no appreciable amount of molecules is present.) One can also compute the cross sections taking account only of the photon and a single atom. We shall use the superscript '0' to characterize the quantities calculated in the low density limit in this manner. Note however that whereas $\sigma_{sJJ'}^{0}(\nu)$ is independent of temperature and density and depends only on the four indicated parameters, $N_{sJ}^{0}$ still depends on temperature and density. Moreover, the phrase "low density limit" is not altogether unambiguous, for two
reasons. First, consider the ionization equilibrium for an atom with one electron, say hydrogen:

\[
\text{H} \leftrightarrow \text{H}^+ + e^-
\]  \hspace{1cm} (2)

According to the mass-action law, as embodied in the Saha equation, as the pressure decreases, the equilibrium shifts farther and farther to the right, so that in the limit of zero pressure no hydrogen atoms would be present at all. In general, all atoms would be completely ionized in the zero density limit (no matter what the temperature might be) if it were possible to reach equilibrium despite the vanishingly small collision rate. The second ambiguity arises from the fact that if one includes the partition functions of the various atoms and ions in the Saha equation, and if one tries to compute these partition functions for an atom in an infinite volume with no other atoms present, then they are divergent sums. For these reasons one can never actually go to the zero density limit, but rather one must always assume a finite number of atoms in a finite volume in order to make the problem physically meaningful.

Now let us suppose that we have computed the low density absorption coefficients

\[
\mu_v^0 = \sum_{s, J, J'} N_{sJ}^0 \sigma_{sJJ'}^0 \langle \psi \rangle
\]  \hspace{1cm} (3)

--correctly subject to the above-mentioned reservations--and we wish to extend the calculation to higher densities by taking account of particle interactions. One might try to do this by finding the correction to \(N_{sJ}^0\) resulting from interactions, likewise the correction to \(\sigma_{sJJ'}^0 \langle \psi \rangle\) resulting from interactions, and then insert the result back into Eq. (1) to compute the correction to \(\mu_v^0\). Since this is what will probably be done in practice, we shall assume this procedure is followed (as applied to \(N_{sJ}\)); but we should at least recognize the fact that this is not the most rigorous way to proceed, and indeed it involves approximations whose magnitude cannot at present be estimated.
The difficulty is of course that as soon as one introduces interatomic forces in the Hamiltonian of the system, \( H \), then one can no longer write \( H \) as a sum of independent parts pertaining to the individual atoms, \( \sum s H_s \). Hence the energy eigenvalues of the system cannot be expressed as sums of the eigenvalues of the individual \( H_s \), and it is no longer strictly meaningful to speak of quantum states \( J \) and \( J' \) of individual atoms as is done in writing down Eq. (1). In particular, it is well known that a plasma can have, in addition to individual excitations, collective excitations ('plasmons' or plasma vibrations). A complete treatment would have to include the effect of all possible excitations of the system as a whole. However, the existing treatments of plasma oscillations generally consider these oscillations separately, and then simply add them to the individual excitations. It is clear that this procedure cannot be rigorously correct, since the number of variables considered is greater than the actual number of degrees of freedom of the system; if some of the system's energy is considered to be assigned to collective modes, then the individual modes must be redefined so that they can be determined by a smaller number of variables.

In the present state of knowledge, such a general treatment does not appear to be feasible for actual calculations; we shall therefore accept the approximation implied in Eq. (1) and consider the individual terms in the sum as if they were independent and only slightly different from their low-density values, reserving collective oscillations for separate treatment. There is still the further assumption to be made that each term in the sum can really be written as a product of two independent factors, an occupation number and a cross-section. If the interactions shift the energy levels \( J \) and \( J' \), and also may affect the probability that a particular state is occupied, then it seems reasonable to suppose that they can also affect the absorption cross sections. While we are not concerned here with the calculation of cross sections, it is suggested that it may be advisable to modify the cross sections by taking account of the physical effects adduced to explain the change of occupation numbers, so that the two parts of the opacity calculation can be made in some sense
consistent with each other. An example of such a modification would be the following: if it is supposed that the presence of a neighboring ion changes the energy of an atomic electron, then presumably the same interaction will distort its wave function and thereby affect the calculation of any matrix element involving that wave function.

The problem under consideration has been approached from various points of view. One may consider the effect of a single perturbing ion at a certain distance from the atom, and determine how the electron will move under the combined fields of the two nuclei; it will need less energy to go over the potential barrier separating it from the perturbing ion than to escape from the atom when no perturbing ion is present, and moreover it may also be able to tunnel through the barrier. Or, instead of a single perturbing ion, there may be a cloud of them shielding the electron from the nucleus, and as a result of the decreased attraction between the nucleus and the electron, the energy needed to remove the latter will be less. In both cases one may conclude that the bottom of the continuum has been lowered, or that the energy levels have been raised. However the former terminology often hides the assumption that all energy levels are shifted equally, which is by no means obviously true. A third approach is to investigate the broadening of spectral lines resulting from the fluctuating microfield in the plasma: when the width of a line is greater than the distance between that line and the continuum, it would appear that some of the electrons in the corresponding energy levels are actually free. Finally, instead of studying the shift of energy levels one may focus attention on the population of these levels, and try to take account of the fact that an electron in a higher level is more vulnerable to the attacks of the environment. It is a confusing feature of the problem that one is not sure whether these are different physical effects which can be calculated separately and then added together, or whether they are merely different ways of looking at the same thing. There is still a need for a general formulation which can encompass all of these aspects, and show how much they overlap.

We have divided the papers cited into two categories, as to whether they
deal principally with the partition function cutoff or the effective ionization potential in a plasma. Papers dealing with both will be included in the latter category. The area of line width and microfield distribution has not been covered; research in these areas, as well as in line shifts, has been reviewed by Lindholm (1942), Margenau & Lewis (1959), Breene (1961), and Baranger (1962). We should point out that the bibliography is not exhaustive; however, it may still prove a convenience to workers in this field. We have occasionally abbreviated ionization potential as I. P., and the lowering of this quantity due to interactions as $\Delta I$.

I. Partition function cutoff.

In the earliest paper we could find, Herzfeld (1916) assumes that the maximum energy allowed in the Bohr model is $-E = e^2/2R_0$, where $R_0 = \text{radius of an orbit}$, which he thinks might be of the order of magnitude of a mean free path. He then discusses statistical mechanical properties of the atom as a function of $R_0$.

Compton and Russell (1924) discuss possible reasons for discrepancies in the populations of excited states of hydrogen in spectra of giant stars; they suggest the possibility of metastable states.

Fermi (1924) and Urey (1924) assume that only such quantum states are possible whose radii are smaller than the average distance between the atoms. Planck treats a quasi-classical partition function for the Bohr atom model. The theories of Fermi and Planck are reviewed by Fowler (1936). Menzel (1933) criticized the Fermi and Planck theories and discussed the effect of collisions and radiation absorption and emission on broadening of upper lines into a continuum; he estimated the effect of radiation by using Einstein's formula for transition probabilities (this effect is now considered negligible compared to
other effects).

Unsöld proposed an extension of Planck's method for calculating the highest principal quantum number, taking account of the perturbation of an excited electron orbit by a single nearby charged particle, or "nearest neighbor." The relation between the theories of Fermi, Planck, and Urey is discussed by Unsöld. Claas (1951) used Unsöld's theory to calculate the probability that an upper level is actually occupied in the presence of neighboring particles. Unsöld's work was extended by Ivanov-Kholodnyi et al. (1960,1961) who also calculated the effect of tunneling of an electron through the potential barrier between one atom and a neighboring one.

Baumann (1958) discusses the partition function cutoff for diatomic molecules; see also the papers of Vardy mentioned below.

Gurvich & Kylividze (1961) discuss a method proposed by Baumann, in a Stuttgart Dissertation which we have not seen. It is proposed that the partition function cutoff can be determined from the uncertainty principle, omitting states for which the interval between two states is less that \( \Delta E = h/\Delta t \). The value of \( \Delta t \) is taken to be about \( 10^{-8} \) seconds, the lifetime for transitions between states with low quantum numbers. Gurvich & Kylividze further assume that the radius of the semi-major axis of the largest permitted orbital must be such that the volume of the atom is less than the average volume per particle; they compare values of the maximum quantum number calculated by several methods.

Woolley (1962) discussed the effect of Debye screening; "an extensive compensation between the bound states just below the continuum and a partial state naucity within the continuum are also noted." In the work of Rouse (1962), "using the charge distribution for a classical Debye atmosphere, it is shown that the maximum bound principal quantum number is essentially the same whether one considers the excited electron
moving in the atmosphere or in a constant central potential due to the same atmosphere." Use of the Debye length and other methods for cutting off the partition function were discussed by McChesney (1964, 1965), Dekeyser (1965), Bowen (1964), Drellishak et al. (1965), Oppenheim & Hafemann (1963), Drawin & Felenenko (1965), and Fauchais & Manson (1965).

Theories of ionization equilibrium based on modified distributions of electrons around nuclei or ions were proposed by Rouse (1964) and Deering (1964).

One way to calculate the maximum quantum number is to replace the Coulomb potential with a Debye shielded potential and solve the Schrödinger equation for the energy levels. This approach has been followed by Ecker & Weizel (1958), Margenau & Lewis (1959), Harris (1962), Hollday et al. (1963), Bonch-Bruevich & Glasko (1963), Smith (1964), Rawls & Shulz (1965), Rouse (1965), and Trubnikov & Yavlinski (1965). The same mathematical problem for a different physical situation was treated by Laurikainen & Euranto (1953) and by Laurikainen & Varho (1958). Friedrichs & Rejto (1962) have recently given a mathematical discussion of perturbations through which a discrete spectrum becomes continuous, which may be applicable to this problem; see also Donoghue (1965). Kulskud (1954) calculated wave functions and matrix elements for a Debye potential. H. Mayer (1947) gives an extensive computational prescription for computing approximate energy level shifts and partition function cutoffs in a very high temperature plasma.

Calculations using partition function cutoffs.

Riewe & Rompe (1938) treated mercury and hydrogen using the Planck theory. Rosa (1948) and Rosa & Unsöld (1948) used Unsöld's theory of the maximum quantum number. Claas (1951) used Unsöld's
method to calculate partition functions of several atoms, and also estimated the relative importance of effects of ions and neutral atoms. Aller et al. (1957) used the Unsöld theory, assuming that the probability that a state is occupied is to be multiplied by a factor: \( \exp(-c p_e n^6) \), where \( p_e \) = electron pressure and \( n \) = quantum number of state. Elste & Jugaku (1957) calculated the partition function of helium and of a hydrogen-helium mixture using Unsöld's assumption that "the active electron cannot remain in its orbit if the potential energy in the combined field of its own nucleus and that of the perturbing ion is equal to the ionization energy." The perturbation of electrons in helium is assumed to be due mainly to protons.

Alpher (1957) assumes that "only those electrons whose classical orbits do not exceed half the mean separation of particles in the gas are counted as bound in the appropriate atom or ion" and uses the Saha equation with this assumption in shock wave calculations. Hester and Sewell (1964) determined the effect of a partition function cutoff on the thermodynamic properties of hydrogen and helium; they found that the results are independent of the cut-off except at high densities. Their method was criticized by McChesney, (1963) who claimed that the Debye-Hückel theory should have been used in the medium-density region.

Limber (1958) assumes that the partition function of a neutral hydrogen atom can be written in the form \( \exp \left(-\left(\frac{\beta a_0}{\hbar}\right)^2\right) \), where \( \hbar \) = Debye length, \( a_0 \) = Bohr radius, and \( \beta \) is an adjustable parameter taken to be about 2. Vardya (1960) follows the method of Limber. Wiese & Griem (1960) use Unsöld's partition function cutoff. Cox & Brownlee (1960) say that "for the higher energy levels we have assumed the levels are hydrogen-like with an effective \( Z \) chosen to give the observed ionization potential. To avoid the divergence of the partition function sum, we have used a cutoff factor similar to that used by Claas" (for
results see Cox (1961)).

The Ecker-Weizel (1958) method was used in calculations by Sherman & Martinek (1961), Kümmler (1960), Hochstim (1961).

Several calculations of thermodynamic properties have been made by using a partition function cutoff criterion based on the Debye length: Drellishak (1964), Drellishak et al. (1963, 1965), Fauchais & Manson (1964), and Bowen (1964). The effect of other methods on thermodynamic-property calculations was discussed by Fauchais & Manson (1965) and Oppenheim & Hafemann (1963).

II. Effective ionization potential in a plasma.

Elenbaas (1937) gives a brief qualitative discussion based on experimental evidence from the high-pressure mercury discharge; later (1947) he uses the quantity $\Delta V_i$ (change in ionization potential) in Unsöld's formula (1938) and finds the value of $\Delta V_i$ needed to achieve agreement with experiment. In his book (1951) Elenbaas gives a survey of experimental data including the effect of pressure on ionization potentials. Rompe & Steenbeck (1939) conclude that the plasma polarization energy given by the Debye-Hückel theory acts to lower the ionization potential, and this effect has been treated quantitatively in many later papers: Timan (1954), Veis (1959, 1960), Siegert (1961), Griem (1962), Brush (1962), McClesney (1963), DeWitt (1965). Since the Debye-Hückel effect increases with density, it may lead to a form of "pressure ionization" which would occur in a classical system, without taking account of the quantum effects that are usually considered responsible for pressure ionization.

Ecker & Weizel (1956) give an approximate solution of the Schrödinger equation with a Debye potential, from which they deduce an energy level shift and a maximum principal quantum number. Their
theory was criticized by Theimer (1957, 1958) who claimed that it is inconsistent with the Debye-Hückel theory; see the replies of Ecker & Weizel (1957, 1958). Duclos & Cambel (1961) and Rother (1958) also discussed the Ecker-Weizel theory.

Quantum field theory (Green's function or diagram expansion) methods have been applied to the calculation of the effect of Coulomb interactions on energy levels by Pargamanik (1961), Pargamanik & Pyatigorsky (1963), Kudrin & Tarasov (1962), DeWitt & Nakayama (1963) and Nakayama & DeWitt (1964). Roberts & Shen (1964) used the Low theory for this purpose.

There have been several attempts to develop theories that can cover, at least approximately, the entire range of densities of practical interest. For high densities, the ion-sphere or Thomas-Fermi theory can be used: see Morse (1940), for calculations of opacity based on the method of Slater (1934) and Slater & Krutter (1935). Duclos and Cambel (1961) formulate a theory which yields for the plasma polarization energy below a critical density, and a result above the critical density which is dominated by the nearest-neighbor interaction. Stewart & Pyatt (1961) give a theory of pressure ionization which yields the Debye result \( \frac{e^2}{D} \) at low density and the nearest-neighbor \( \frac{e^2}{r_0} \) or ion-sphere result and high density, and passes continuously as a function of density and temperature between these limits, rather than discontinuously shifting from one result to the other at a critical density as in the theory of Duclos & Cambel (1961). Keller & Meyerott (1952) modify the ion-sphere method to allow the nuclei to have a statistical distribution in space, as well as the electrons; the ionization potential of the electrons is lowered because the ionized electron does not go off to an infinite distance but joins the free electron shield around the ion. Ecker & Krüll derive a result
for ΔI similar to that given by Duclos and Cambel. H. R. Griem (1964) in his book *Plasma Spectroscopy* (Chapter 6) gives an extensive discussion of the lowering of the ionization potential, and compares the results of calculations using the nearest-neighbor (e²/r₀) and Debye theory (e²/D) results. See also the book by Traving (1960).

Olsen (1961) gives experimental data for ΔI and radiation intensities in an argon plasma, and compares his experimental results with theory using the various theoretical predictions for ΔI. Garton, Parkinson, & Reeves (1962) have apparently directly observed the I. P. lowering by means of what they term "forced autoionization" of states which lie below the vacuum series limit, but above the lowered series limit which appears in a plasma of moderate to high density (see also Garton et al. (1964)). The theory presented by Brunner (1960) has been criticized by Ecker & Kröll (1963) and by Olsen (1961) on the grounds that he counts the lattice interaction term twice. Further experimental references can also be found in the paper by Ecker & Kröll (1963). Berthelot (1965) suggests a method for the experimental determination of the lowering of the ionization potential by measuring the ratio of the intensities of two spectrum lines belonging to adjacent stages of ionization of a given atom.

Vardy (1960) called attention to the significance of the lowering of the ionization potential for molecular gases of astrophysical interest. In two subsequent papers (Vardy, 1965a, 1965b) he has computed partition functions and thermodynamic properties of H₂ and H₂⁺ using a method related to the Unsöld nearest-neighbor approach.

We should mention, at least briefly, the problem of the merging and/or disappearance of high lines in a series prior to the series limit. This problem is somewhat similar to the problems of the partition function cutoff and the lowering of the ionization potential, although
most authors consider it to be a distinct and independent problem (Olsen 1961). Sugita (1934) treated the effect of collisions on the width of lines, and from this effect calculated a relation between the quantum number at which merging occurs and the electron density. Inglis & Teller (1939) used the Holtsmark theory for the mean electric field to obtain another version of this relation; while they criticized some of Sugita's assumptions, they agree with him that the Stark effect is more important than the collision effect. The Inglis-Teller relation has proved very useful because of its simplicity and wide applicability. Armstrong (1964) has shown that the Inglis-Teller relation properly accounts for the positions of the "photoelectric edges" as observed by Boldt (1959) in nitrogen and oxygen.

We mention briefly some other recent papers: Larenz (1963) proposed a theory in which the density distribution of states changes continuously on going from bound to free states; Ecker & Krüll (1965) discuss lowering of the ionization energy in a plasma with different temperatures of the components; Hochstim (1963) reviews methods of calculation of thermodynamic properties, including Coulomb corrections; Maitland & Dunn (1963) discuss thermal ionization in a system with a distribution of ionization potentials resulting from Stark effects. Calculations of thermodynamic properties, including Debye-Hückel effects and lowering of ionization potentials, are presented by Hilsenrath & Klein (1963, 1964, 1965); McChesney & Jones (1965); Patch (1961); Fauchais & Manson (1965); Artmann (1965); Hochstim & Terhune (1963); Artmann & Bohn (1965).
REFERENCES


Drellishak, K. S. (1964): Partition functions and thermodynamic properties of high-temperature gases, Northwestern University, Gas Dynamics Laboratory, report AEDC-TDR-64-22.


Air Force Special Weapons Center Report AFSWC TR-61-72 (Section 2,1).