Aus unserer in Abb. 2 dargestellten Funktion $m(n_0)$ (ausgezogene Kurve) ist zu sehen, daß $m(n_0)$ bei $n_0 = 8{,}4 \cdot 10^{15}$ g cm^{-3} ein Maximum aufweist und nach Durchschreiten dieses Maximums mit wachsendem n_0 ziemlich rasch abfällt. Es existiert also eine dem Maximum entsprechende kritische Masse m_c, oberhalb der ein Neutronenstern nicht existieren kann. Aus der von uns berechneten Kurve $m(n_0)$ ergibt sich $m_c = 0{,}96\, m_\odot$, wo wir, wie üblich, mit $m_\odot$ die Sonnenmasse bezeichneten.

In Abb. 2 ist auch die von OPPENHEIMER und VOLKOFF[5] berechnete Funktion $m(n_0)$ dargestellt, die diese Autoren mit der Annahme erhielten, daß zwischen den Neutronen keinerlei Wechselwirkung besteht. Der Verlauf der von OPPENHEIMER und VOLKOFF berechneten Funktion ist ähnlich wie der der von uns berechneten Funktion; für die kritische Masse erhielten sie $m_c = 0{,}66\, m_\odot$, also einen Wert, der in der Nähe des von uns berechneten Wertes liegt.

Free-Bound Model of the Plasma in Equilibrium *

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The plasma in thermodynamic equilibrium has been extensively discussed under the assumption that all particles can be classified as "bound" or "classically 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. On the basis of a quantum-mechanical treatment we develop an "adapted free-bound approximation" for the eigenstates and a classical approximation for the partition function of the free particles. It is a decisive feature of the analysis that it takes free-bound interaction into account. The results produce values for the free-bound limit and the limit of the series continuum. They also remove the divergence difficulties.

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,

Divergencies of the classical partition function of free electrons and protons.

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[1]. A much stronger limitation was introduced by the omission of eigenstates extending beyond the next

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* Part of this work was carried out during our stay at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado.

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[1] M. PLANCK, Ann. Phys. **75**, 637 [1924].

neutral neighbour [2–5]. If the influence of the nearest ionic neighbour is assumed to dominate, then only eigenstates with an energy $\varepsilon < -3\,e^2/r_0$ 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 [6].

The simultaneous average interaction of the electrons and ions can be taken into account by solving the SCHRÖDINGER equation with the DEBYE potential [7]. As was pointed out (l. c.) this procedure is valid for the highly excited states only and yields an upper limit $\varepsilon_b < -e^2/D$ for the eigenstates (D – DEBYE length). Essentially the same result has been derived on the basis of a perturbation theory [8] and under the assumption that the atomic electron experiences a constant potential shift due to the free particles [9].

Level shift and broadening. 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 separation of consecutive terms. Using this concept it was stated that all levels with

$$\varepsilon_h > -(e^2/r_0)\,(r_0/a_0)^{1/5}$$

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 $-e^2/D$.

A recent investigation [13] calculates the shift and broadening of the energy levels including non-stationary 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 occuring 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].

Classification and Terminology

It will prove suitable to classify all particles of the system in the following energy scale (ε – scale): A particle is labeled with ε, if the value of its pair energy with the nearest oppositely charged neighbour in their center of gravity system is ε, – neglecting all other interactions.

We distinguish two particle groups: free particles (f) and bound particles (b). Within the free group we distinguish the subgroup of quasi-free states (q f). They 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 distinguish the bound-hydrogenlike (h) states. They 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 ε-scale are denoted by ε_h, ε_b and ε_f as shown in Fig. 1.

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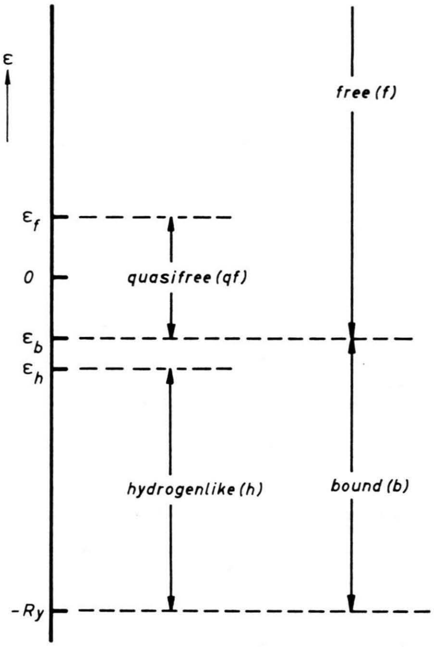

Fig. 1. Schematic representation of the terminology and definitions used in the text.

Aim of this Investigation

All the investigations quoted in the previous section use the free-bound approximation which postulates that all particles can be classified in two groups, bound particles and classically describable free particles. Within this classification the lack of understanding and the discrepancies indicated above are – in our opinion – due to an incorrect ad hoc demarcation of the free and bound states and the hydrogenlike and non-hydrogenlike states. Consequently we aim to contribute to the resolution of the difficulties by determining these demarcations from a systematical quantum-mechanical treatment. The essential feature of this treatment is the incorporation of the free-bound interaction.

In doing so we develop the "adapted free-bound approximation" described in the following section. That means we stay within the frame of the classification in free and bound particles since it describes the large majority of the particles correctly and has been widely applied in the literature. We are well aware that there are particles which do not exactly fit in any of these two groups.

The questions which we want to answer from our analysis are:

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

II. Up to what limit (ε_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?

Adapted Free-Bound Approximation

Definition: In accord with the general use in the literature our "adapted free-bound model" admits only two types of particle states: free and bound ones.However , in contrast to the naive free-bound limit $\varepsilon = 0$ it applies the following definition of free and bound:

Consider the particle 1 and the quantity

$$G_{1\nu} = \int \Psi\, \Psi^* \,|\, \boldsymbol{r}_1 - \boldsymbol{r}_\nu \,|\, \mathrm{d}\boldsymbol{r}$$

where the index ν 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 Γ-space.

Then particle 1 is considered bound if there exists a number (k) with

$$G_{1k} \ll G_{1\nu} \quad \text{for all} \quad \nu \neq k\,.$$

Particle 1 is considered to be free if such a number (k) does not exist. – Physically this means that the 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.

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

Analysis: The eigenfunction Ψ and eigenvalues E of our system are determined by the equation

$$H\, \Psi_{m\mathbf{p}} = E_{m\mathbf{p}}\, \Psi_{m\mathbf{p}} \tag{1}$$

where H denotes the HAMILTON operator of the whole system and m represents the set of the discrete, $\mathbf{p}$ the continuous quantum numbers.

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

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 ε-value is positive or negative.

The zero order eigenfunction is then

$$\Psi^{(0)}_{m\mathbf{P}} = \Big[\frac{1}{(N!)^2} \sum_j (-1)^{|\mathscr{P}_j|} \mathscr{P}_j \Big\{ \prod_i \exp\{(i/\hbar)\, \boldsymbol{p}_i \boldsymbol{r}_i\} \prod_l \Phi_l(\xi_l) \exp\{(i/\hbar)\, \boldsymbol{P}_l \boldsymbol{R}_l\} \Big\} \Big]_{m\mathbf{P}} \tag{2}$$

where ξ_l and $\boldsymbol{R}_l$ are the relative and center of gravity coordinate of the bound state (l). $\boldsymbol{r}_i$ and $\boldsymbol{p}_i$ are resp. the coordinates and momenta of the free particles, Φ_l is the hydrogen eigenfunction with the quantum number ν_{lm} and the eigenvalue ε_l, N is the total number of electrons or ions. $\mathscr{P}_j$ is the set of permutation operators covering all exchanges between all identical particles. $|\mathscr{P}_j|$ denotes the number of corresponding transpositions.

For simplicity we omit in the following the indices of the total eigenstate $(m\,\boldsymbol{p})$, 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.

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

$$\hat{H} = \hat{H}_{\mathrm{I}} + \hat{H}_{\mathrm{II}} + \hat{H}^* \tag{3}$$

with

$$\hat{H}_{\mathrm{I}} = -(\hbar^2/2) \sum_i (\Delta_i/m_i), \tag{4}$$

$$\hat{H}_{\mathrm{II}} = \sum_l{}^{(\mathrm{II})}\, \hat{H}_l = \sum_l{}^{(\mathrm{II})} \Big\{ -\frac{\hbar^2}{2} \Big(\frac{\Delta_{l+}}{m_+} + \frac{\Delta_{l-}}{m_-} \Big) - \frac{e^2}{|\boldsymbol{r}_{l+} - \boldsymbol{r}_{l-}|} \Big\} \tag{5}$$

$$\begin{aligned} \hat{H}^* &= \sum_l{}^{(\mathrm{II})}\, V_{l\mathrm{I}} + \tfrac{1}{2} \sum_{l,k}{}'^{(\mathrm{II})}\, V_{lk} + \tfrac{1}{2} \sum_{i,j}{}'^{(\mathrm{I})}\, V_{ij} \\ &= e \sum_l{}^{(\mathrm{II})} \Big\{ \sum_i{}^{(\mathrm{I})} \Big(\frac{e_i}{|\boldsymbol{r}_{l+} - \boldsymbol{r}_i|} - \frac{e_i}{|\boldsymbol{r}_{l-} - \boldsymbol{r}_i|} \Big) + \frac{e}{2} \sum_k{}^{(\mathrm{II})} \Big(\frac{1}{|\boldsymbol{r}_{l+} - \boldsymbol{r}_{k+}|} - \frac{1}{|\boldsymbol{r}_{l-} - \boldsymbol{r}_{k+}|} - \frac{1}{|\boldsymbol{r}_{l+} - \boldsymbol{r}_{k-}|} + \frac{1}{|\boldsymbol{r}_{l-} - \boldsymbol{r}_{k-}|} \Big) \Big\} \\ &\quad + \tfrac{1}{2} \sum_{i,j}{}^{(\mathrm{I})} \frac{e_i\, e_j}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \end{aligned} \tag{6}$$

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

$$E^{(0)} = \sum_i \frac{p_i^2}{2\, m_i} + \sum_l{}^{(\mathrm{II})} \Big(\varepsilon_l + \frac{P_l^2}{2\, M} \Big) \quad \text{with } M = m_+ + m_-. \tag{7}$$

The first order perturbation is governed by the equation

$$(\hat{H}_{\mathrm{I}} + \hat{H}_{\mathrm{II}})\, \Psi^{(1)} - E^{(0)}\, \Psi^{(1)} = - \sum_l{}^{(\mathrm{II})} V_{l\mathrm{I}}\, \Psi^{(0)} - \tfrac{1}{2} \sum_{l,k}{}' V_{lk}\, \Psi^{(0)} - \tfrac{1}{2} \sum_{i,j}{}^{(\mathrm{I})}\, V_{ij}\, \Psi^{(0)}. \tag{8}$$

We use

$$E^{(1)} = \sum E^{(1)}_{l\mathrm{I}} + E^{(1)}_{\mathrm{I}} + E^{(1)}_{\mathrm{II}} \tag{9}$$

where the energy $E^{(1)}_{l\mathrm{I}}$ is the perturbation energy due to the interaction of the pair (l) with all particles of group I, whereas $E^{(1)}_{\mathrm{I}}$ and $E^{(1)}_{\mathrm{II}}$ account for the interaction within the groups I and II respectively. Up to the first order we represent the eigenfunctions in the form

$$\Psi = \Psi^{(0)} + \sum_l{}^{(\mathrm{II})}\, \Psi^{(1)}_{l\mathrm{I}} + \Psi^{(1)}_{\mathrm{I}} + \Psi^{(1)}_{\mathrm{II}} \tag{10}$$

where $\Psi^{(1)}_{l\mathrm{I}}$, $\Psi^{(1)}_{\mathrm{I}}$ and $\Psi^{(1)}_{\mathrm{II}}$ satisfy the equations

$$\begin{aligned} &(\hat{H}_{\mathrm{I}} + \hat{H}_{\mathrm{II}})\, \Psi^{(1)} - E^{(0)}\, \Psi^{(1)} \\ &\quad = - \sum_l{}^{(\mathrm{II})}\, V_{l\mathrm{I}}\, \Psi^{(0)} - \tfrac{1}{2} \sum_{l,k}{}' V_{lk}\, \Psi^{(0)} + E^{(1)}\, \Psi^{(0)} \end{aligned} \tag{11}$$

and

$$\begin{aligned} &(\hat{H}_{\mathrm{I}} + \hat{H}_{\mathrm{II}})\, \Psi^{(1)}_{\mathrm{I}} - E^{(0)}\, \Psi^{(1)}_{\mathrm{I}} \\ &\quad = - \tfrac{1}{2} \sum_{i,j}{}' V_{ij}\, \Psi^{(0)} + E^{(1)}_{\mathrm{I}} \Psi^{(0)}, \end{aligned} \tag{12}$$

$$\begin{aligned} &(\hat{H}_{\mathrm{I}} + \hat{H}_{\mathrm{II}})\, \Psi^{(1)}_{\mathrm{II}} - E^{(0)}\, \Psi^{(1)}_{\mathrm{II}} \\ &\quad = - \tfrac{1}{2} \sum_{l,k}{}'^{(\mathrm{II})}\, V_{lk}\, \Psi^{(0)} + E^{(1)}_{\mathrm{II}} \Psi^{(0)}. \end{aligned} \tag{13}$$

We consider the contribution $\Psi^{(1)}_{l\mathrm{I}}$ which describes the change of the eigenfunction due to the interaction of the pair l with the "free" particles of group I. We use the development

$$\Psi^{(1)}_{l\mathrm{I}} = \sum_s \int a_{s\mathbf{p}'}\ \Psi^{(0)}_{s\mathbf{p}'}\, \mathrm{d}\mathbf{p}' \tag{14}$$

where the symbol $\mathbf{p}$ stands as well for the set of continuous quantum numbers $(\boldsymbol{p})$ of the free particles as for the parameters $(\boldsymbol{P})$ describing the translation of the pairs of group II.

Using the relation

$$\int \Psi^{(0)}_{s\mathbf{p}'}\, \Psi^{(0)}_{m\mathbf{p}'}\, \mathrm{d}\boldsymbol{r} = \delta(\mathbf{p}-\mathbf{p}')\, \delta_{ms} \tag{15}$$

the coefficient $a_{s\mathbf{p}}$ follows from (11) to be

$$a_{s\mathbf{p}'} = \frac{E^{(1)}_{l\mathrm{I}}\, \delta(\mathbf{p}-\mathbf{p}')\, \delta_{ms} - V_{sm\mathbf{p}'\mathbf{p}}}{E^{(0)}{}_{s\mathbf{p}'} - E^{(0)}{}_{m\mathbf{p}}} \tag{16}$$

with

$$V_{sm\mathbf{p}'\mathbf{p}} = \int \Psi^{(0)*}_{s\mathbf{p}'}\, V_{l\mathrm{I}}\, \Psi^{(0)}_{m\mathbf{p}}\, \mathrm{d}\boldsymbol{r}\,. \tag{17}$$

According to the perturbation theory of continuous systems[18] this requires $E^{(1)}_{\mathrm{I}} = 0$ and we have therefore

$$\Psi^{(1)}_{l\mathrm{I}} = -\sum_{s} \frac{V_{sm\mathbf{p}'\mathbf{p}}\, \Psi^{(0)}{}_{s\mathbf{p}'}\, \mathrm{d}\mathbf{p}'}{E^{(0)}{}_{s\mathbf{p}'} - E^{(0)}{}_{m\mathbf{p}}}\,. \tag{18}$$

Using $V_{1\mathrm{I}}$ from Eq. (6) we have

$$V_{sm\mathbf{p}'\mathbf{p}} = \sum_i e\, e_i \int \Psi^{(0)*}_{s\mathbf{p}'} \left(\frac{1}{|\boldsymbol{r}_{l+} - \boldsymbol{r}_i|} - \frac{1}{|\boldsymbol{r}_{l-} - \boldsymbol{r}_i|} \right) \Psi^{(0)}_{m\mathbf{p}}\, \mathrm{d}\boldsymbol{r}\,. \tag{19}$$

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

$$\begin{aligned}\overline{V}_{l,i} = e\, e_i \prod^{j\neq i,\, \sigma \neq l} \delta(\boldsymbol{p}_j' - \boldsymbol{p}_j)\, \delta(\boldsymbol{P}_\sigma' - \boldsymbol{P}_\sigma) \prod^{k \neq l} \delta_{\nu_{ks},\, \nu_{km}} \\ \times \int \exp\{-(i/\hbar)\, [\boldsymbol{R}_l(\boldsymbol{P}_l' - \boldsymbol{P}_l) + \boldsymbol{r}_i(\boldsymbol{p}_i' - \boldsymbol{p}_i)]\} \left(\frac{1}{|\boldsymbol{r}_{l+} - \boldsymbol{r}_i|} - \frac{1}{|\boldsymbol{r}_{l-} - \boldsymbol{r}_i|} \right) \Phi_{\nu_{ls}}(\boldsymbol{\xi}_l)\, \Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)\, \frac{\mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{R}_l\, \mathrm{d}\boldsymbol{\xi}_l}{h^6}\end{aligned} \tag{20}$$

and

$$\begin{aligned}\tilde{V}_{l,i} = e\, e_i \prod^{j\neq i,\, \sigma \neq l} \delta(\boldsymbol{p}_j' - \boldsymbol{p}_j)\, \delta(\boldsymbol{P}_\sigma' - \boldsymbol{P}_\sigma) \prod^{k \neq l} \delta_{\nu_{ks},\, \nu_{km}} \\ \times \int \exp\{-(i/\hbar)\, (\boldsymbol{R}_i \boldsymbol{P}_i' - \boldsymbol{R}_l \boldsymbol{P}_l + \boldsymbol{r}_l \boldsymbol{p}_l' - \boldsymbol{r}_i \boldsymbol{p}_i)\} \left(\frac{1}{|\boldsymbol{r}_{l+} - \boldsymbol{r}_i|} - \frac{1}{|\boldsymbol{r}_{l-} - \boldsymbol{r}_i|} \right) \Phi_{\nu_{ls}}(\boldsymbol{\xi}_i)\, \Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)\, \frac{\mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{R}_l\, \mathrm{d}\boldsymbol{\xi}_l}{h^6}\end{aligned} \tag{21}$$

Let us first consider the terms $V_{l,i}$. We develop $V_{l,i}$ in a power series with respect to $\boldsymbol{\xi}_l$ and restrict ourselves to the first order term

$$V_{l,i} = e\, e_i \frac{(\boldsymbol{R}_l - \boldsymbol{r}_i)\, \boldsymbol{\xi}_l}{(\boldsymbol{R}_l - \boldsymbol{r}_i|^3}\,. \tag{22}$$

The justification for this procedure is given below. Introducing Eq. (22) into Eq. (19) and using the abbreviations

$$D_{j\sigma} = \prod \delta(\boldsymbol{p}_j' - \boldsymbol{p}_j)\, \delta(\boldsymbol{P}_\sigma' - \boldsymbol{P}_\sigma), \quad \Delta\boldsymbol{p}_i = \boldsymbol{p}_i' - \boldsymbol{p}_i, \quad \Delta\boldsymbol{P}_l = \boldsymbol{P}_l' - \boldsymbol{P}_l \tag{23}$$

we obtain

$$\overline{V}_{l,i} = D_{j\sigma}\, e\, e_i \langle \nu_{ls} | \boldsymbol{\xi} | \nu_{lm} \rangle \int \frac{(\boldsymbol{R}_l - \boldsymbol{r}_i)}{|\boldsymbol{R}_l - \boldsymbol{r}_i|^3} \exp\{-(i/\hbar)\, (\boldsymbol{r}_i \Delta\boldsymbol{p}_i + \boldsymbol{R}_l \Delta\boldsymbol{P}_l)\}\, \frac{\mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{R}_l}{h^6} \tag{24}$$

where $\langle \nu_{ls} | \boldsymbol{\xi} | \nu_{lm} \rangle$ is the quantum-mechanical dipol moment. The evaluation of the integral produces

$$\overline{V}_{l,i} = i\, e\, e_i \frac{D_{j\sigma}}{h^3}\, 4\pi \langle \nu_{ls} | \boldsymbol{\xi} | \nu_{lm} \rangle \cos\Theta_1\, \delta(\Delta\boldsymbol{P}_l + \Delta\boldsymbol{p}_i)\, \frac{\hbar}{|\Delta\boldsymbol{p}_i|} \tag{25}$$

where Θ_1 is the angle between $\langle \nu_{ls} | \boldsymbol{\xi} | \nu_{lm} \rangle$ and $\Delta\boldsymbol{p}_i$. Introducing Eq. (25) into Eq. (18) we find

$$_{\overline{V}}\Psi^{(1)}_{l\mathrm{I}} = i\, e \sum_s \sum_i e_i\, 4\pi \langle \nu_{ls} | \boldsymbol{\xi} | \nu_{lm} \rangle\, \hbar\, \frac{\Psi^{(0)}{}_{m\mathbf{p}}}{h^3} \cdot \frac{\Phi_{\nu_{ls}}}{\Phi_{\nu_{lm}}} \int \frac{\exp\{(i/\hbar)\, \Delta\mathbf{p}_i(\boldsymbol{r}_i - \boldsymbol{R}_l)\}}{|\Delta\mathbf{p}_i|\, \{\Delta\varepsilon + \Delta\mathbf{p}_i \cdot \boldsymbol{v}_r + |\Delta\mathbf{p}_i|^2/2\mu\}} \cos\Theta_1\, \mathrm{d}\boldsymbol{p}_i' \tag{26}$$

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[18] D. J. Blochinzew, Grundlagen der Quantenmechanik, Deutscher Verlag der Wissenschaften, Berlin 1961.

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

$\Delta\varepsilon$ is the change in the excitational energy and the abbreviations

$$\boldsymbol{v}_r = \boldsymbol{p}_i/m_i - \boldsymbol{P}_l/M \quad \text{and} \quad 1/\mu = 1/m_i + 1/M \tag{27}$$

are used.

An exact evaluation of this integral is extremely involved and definitely beyond the scope of this paper. Transparent results are obtained only if the bracket in the denominator of the integrand is independent of $\boldsymbol{p}_i'$. At least this should be secured in the range where the frequency in the nominator is not high enough to cancel the contributions to the integral.

That means we should have

$$p_i'\, a/\hbar \gg 1 \tag{28}$$

for all p_i', which do not satisfy the conditions

$$|p_i'|^2 \ll |B|, \qquad 2\,|p_i'|\,|q| \ll |B|$$

with

$$\boldsymbol{q} = \boldsymbol{p}_i\left(\frac{\mu}{m_i} - 1\right) - \boldsymbol{P}_l\,\frac{\mu}{M_l},$$

$$B = 2\,\mu\left\{\Delta\varepsilon + p_i^2\left(\frac{1}{2\,\mu} - \frac{1}{m_i}\right) + \frac{\boldsymbol{p}_i\,\boldsymbol{P}_l}{M_l}\right\}.$$

In the following it is advised to distinguish between electrons and ions.

Electrons:

We neglect all terms of the order m_-/m_+ and distinguish the two cases

$$|\Delta\varepsilon| \ll p_-^2/2\,m_-, \qquad |\Delta\varepsilon| \gg p_-^2/2\,m_- \tag{29}$$

for which condition (28) reads

$$a\,p_-/\hbar \gg 1, \qquad a\cdot\sqrt{2m\,\Delta\varepsilon}/\hbar \gg 1 \tag{30}$$

and the amplitude of the perturbation is respectively

$$A \sim 2\,m_-/p_-^2, \qquad A \sim 1/\Delta\varepsilon. \tag{31}$$

Ions:

Here we distinguish the two cases

$$|\Delta\varepsilon| \ll (p_+/m_+)\sqrt{2\,m_+\,k\,T},$$
$$|\Delta\varepsilon| \gg (p_+/m_+)\sqrt{2\,m_+\,k\,T} \tag{32}$$

for which the condition (28) reads

$$(a/\hbar)\sqrt{p_+\sqrt{2\,m_+\,k\,T}} \gg 1,$$
$$a\sqrt{2\,m_+\,\Delta\varepsilon}/\hbar \gg 1 \tag{33}$$

with the amplitudes

$$A \sim m_+/(p_+\sqrt{2\,m_+\,k\,T}), \quad A \sim 1/\Delta\varepsilon. \tag{34}$$

For all four cases of the electrons and ions the bracket in the denominator of the integrand of (26) is constant and consequently we are able to carry out the integration with respect to $\boldsymbol{p}_i'$ producing the perturbation as a function of the momentum $\boldsymbol{p}_i$ and the interparticle distance (a).

Two points should now be observed. First we are not interested in the perturbation for a special value of $\boldsymbol{p}_i$ and a distance (a) but rather in the average perturbation which is typical for our system in equilibrium. Second the conditions (28) – (34) do not have to be fulfilled for all possible particle states but only for the majority of the states close to the most probable state.

Carrying out the corresponding averaging processes we find as a sufficient condition

$$\sqrt{r_0\,r_\mathrm{w}} > \lambda \quad \text{with} \quad r_\mathrm{w} = e^2/k\,T, \; \lambda = h/\sqrt{2\,\pi\,m\,k\,T} \tag{35}$$

and the following results:
In the range $\Delta\varepsilon \ll k\,T$

$$_V\Psi_{l\mathrm{I}}^{(1)} = \Psi_{m\mathbf{p}}^{(0)}\,\frac{\Phi_{\nu_{ls}}(\boldsymbol{\xi}_l)}{\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)}\,\frac{e^2}{r_0^2}\,\langle \nu_{ls}\,|\,\xi\,|\,\nu_{lm}\rangle\,\frac{1}{\Delta\varepsilon}. \tag{36}$$

In the range $\Delta\varepsilon \gg k\,T$

$$_V\Psi_{l\mathrm{I}}^{(1)} = \Psi_{m\mathbf{p}}^{(0)}\,\frac{\Phi_{\nu_{ls}}(\boldsymbol{\xi}_l)}{\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)}\,\frac{e^2}{r_0^2}\,\langle \nu_{ls}\,|\,\xi\,|\,\nu_{lm}\rangle\,\frac{1}{k\,T}. \tag{37}$$

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 $\Delta\varepsilon$ denotes the transition to the next neighbouring state.

Let us now consider the terms $V_{l,i}$ where the index (i) denotes a perturbing ion[19]. We must first express the quantities $\boldsymbol{r}_{l+}$, $\boldsymbol{r}_{l-}$, $\boldsymbol{\xi}_i$ and $\boldsymbol{R}_i$ in Eq. (21) in terms of $\boldsymbol{\xi}_l$, $\boldsymbol{R}_l$ and $\boldsymbol{r}_i$ by the relations

$$\boldsymbol{r}_{l+} = \boldsymbol{R}_l - (m_-/M)\,\boldsymbol{\xi}_l; \qquad \boldsymbol{r}_{l-} = \boldsymbol{R}_l + (m_+/M)\,\boldsymbol{\xi}_l;$$
$$\boldsymbol{\xi}_i = (m_+/M)\,\boldsymbol{\xi}_l + \boldsymbol{R}_l - \boldsymbol{r}_i;$$
$$\boldsymbol{R}_i = (m_+/M)\,\boldsymbol{r}_i + (m_-/M)\,\boldsymbol{R}_l + (m_+\,m_-/M^2)\,\boldsymbol{\xi}_l. \tag{38}$$

Introducing further the ariables $\boldsymbol{\eta}_1, \boldsymbol{\eta}_2$ by

$$\boldsymbol{r}_i = \tfrac{1}{2}(\boldsymbol{\eta}_1 + \boldsymbol{\eta}_2), \qquad \boldsymbol{R}_l = \tfrac{1}{2}(\boldsymbol{\eta}_1 - \boldsymbol{\eta}_2) \tag{39}$$

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[19] An estimate of the corresponding term with a perturbing electron shows that the ion term considered here is representative.

and performing the integration over $\boldsymbol{\eta}_1$ we arrive at

$$\tilde{V}_{l,i} = e\,e_i (D_{j\sigma}/h^3)\,\delta(\boldsymbol{p}_i+\boldsymbol{P}_l-\boldsymbol{P}_i'-\boldsymbol{p}_l') \int \exp\{(i/\hbar)\,(\boldsymbol{\Lambda}_1\boldsymbol{\xi}_l+\boldsymbol{\Lambda}_2\boldsymbol{\eta}_2)\}\,\Phi^*_{\nu_{is}}(\boldsymbol{\xi}_i) \left(\frac{1}{|\boldsymbol{\eta}_2-(m_-/M)\,\boldsymbol{\xi}_l|}-\frac{1}{|\boldsymbol{\eta}_2+(m_+/M)\,\boldsymbol{\xi}_l|}\right)\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)\,\frac{\mathrm{d}\boldsymbol{\xi}_l\,\mathrm{d}\boldsymbol{\eta}_2}{h^3} \tag{40}$$

with

$$\boldsymbol{\Lambda}_1=\frac{m_-}{M}\left(\boldsymbol{p}_l'-\frac{m_+}{M}\boldsymbol{P}_i'\right),\qquad \boldsymbol{\Lambda}_2=\frac{1}{2}\left(\boldsymbol{p}_l'+\boldsymbol{p}_i-\boldsymbol{P}_l-\left(\frac{m_+-m_-}{M}\right)\boldsymbol{P}_i'\right). \tag{41}$$

Using Eqs. (40) and (41) in Eq. (18) and carrying out the integrations wiht respect to $D_{i\sigma}$ we find

$$\begin{aligned}{}_{\tilde{V}}\Psi^{(1)}_{l\mathrm{I}}=\sum_i\sum_s e\,e_i\,\Psi^{(0)}_m\Bigg[\frac{\Phi_{\nu_{is}}(\boldsymbol{\xi}_i)}{\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)}\int\frac{\exp\{(i/\hbar)\,(-\boldsymbol{P}_l\boldsymbol{R}_l-\boldsymbol{p}_i\boldsymbol{r}_i+\boldsymbol{p}'_l\boldsymbol{r}_l+\boldsymbol{P}'_i\boldsymbol{R}_i)\}}{\Delta\varepsilon+(P_i'^2-P_l^2)/2\,M+(p_l'^2-p_i^2)/2\,m_+}\,\delta(\boldsymbol{p}_i+\boldsymbol{P}_l-\boldsymbol{P}_i'-\boldsymbol{p}_l')\\ \times\left\{\int\Phi^*_{\nu_{is}}(\boldsymbol{\xi}_i)\,\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)\exp\{(i/\hbar)\,(\boldsymbol{\Lambda}_1\boldsymbol{\xi}_l+\boldsymbol{\Lambda}_2\boldsymbol{\eta}_2)\}\left(\frac{1}{|\boldsymbol{\eta}_2-(m_-/M)\,\boldsymbol{\xi}_l|}-\frac{1}{|\boldsymbol{\eta}_2+(m_+/M)\,\boldsymbol{\xi}_l|}\right)\mathrm{d}\boldsymbol{\xi}_l\mathrm{d}\boldsymbol{\eta}_2\,\frac{\mathrm{d}\boldsymbol{P}_i'\,\mathrm{d}\boldsymbol{p}_l'}{h^6}\Bigg]\end{aligned} \tag{42}$$

where it should be remembered that in $\Phi^*_{\nu_{is}}(\boldsymbol{\xi}_i)$ the coordinate $\boldsymbol{\xi}_i$ should be expressed by $\boldsymbol{\xi}_l$, $\boldsymbol{R}_l$ and $\boldsymbol{r}_i$ as given in Eq. (38). We evaluate Eq. (42) in the same approximation as Eq. (26). Performing the integration with respect to $\boldsymbol{P}_i$ eliminating at the same time $\boldsymbol{r}_{l+}$ and $\boldsymbol{R}_i$ using the Eqs. (38) we obtain

$$\begin{aligned}{}_{\tilde{V}}\Psi^{(1)}_{l\mathrm{I}}=\sum_i\sum_s e\,e_i\,\Psi^{(0)}_{m\mathbf{p}}\Bigg[\frac{\Phi_{\nu_{is}}(\boldsymbol{\xi}_i)}{\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)}\int\exp\{-(i/\hbar)\,\Delta\boldsymbol{r}\,\Delta\boldsymbol{p}_l\}\int\frac{\exp\{(i/\hbar)\,\boldsymbol{\eta}_2\boldsymbol{p}_l\}}{\Delta\varepsilon}\,\Phi^*_{\nu_{is}}(\boldsymbol{\xi}_i)\,\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)\\ \left(\frac{1}{|\boldsymbol{\eta}_2|}-\frac{1}{|\boldsymbol{\eta}_2-\boldsymbol{\xi}_l|}\right)\mathrm{d}\boldsymbol{\xi}_l\,\mathrm{d}\boldsymbol{\eta}_2\,\frac{\mathrm{d}(\Delta\boldsymbol{p}_l)}{h^3}\Bigg]\end{aligned} \tag{43}$$

where we have neclected terms of the order m_-/m_+ and applied the abbreviation $\Delta\boldsymbol{p}_l=\boldsymbol{p}_l-\boldsymbol{P}_l$. Integrating first with respect to $\Delta\boldsymbol{p}_l$ *and then over* $\boldsymbol{\eta}_2$ we finally have

$${}_{\bar{V}}\Psi^{(1)}_{l\mathrm{I}}=\sum_i\sum_s e\,e_i\,\Psi^{(0)}_{m\mathbf{p}}\left[\frac{\Phi_{\nu_{is}}(\boldsymbol{\xi}_i)}{\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)}\int\frac{\Phi^*_{\nu_{is}}(\boldsymbol{\xi}_l-\Delta\boldsymbol{r})}{\Delta\varepsilon}\,\Phi_{\nu_{lm}}(\boldsymbol{\xi}_l)\left(\frac{1}{|\Delta\boldsymbol{r}|}-\frac{1}{|\Delta\boldsymbol{r}+\boldsymbol{\xi}_l|}\right)\mathrm{d}\boldsymbol{\xi}_l\right]. \tag{44}$$

The total effect of the free-bound interaction on the eigenfunctions represents itself as the sum over the contributions of the type ${}_{\bar{V}}\Psi^{(1)}_{l\mathrm{I}}$ and ${}_{\tilde{V}}\Psi^{(1)}_{l\mathrm{I}}$ given in Eqs. (36), (37) and (44) respectively.

The perturbations $\Psi^{(1)}_{\mathrm{II}}$ and $\Psi^{(1)}_{\mathrm{I}}$ 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[20]. The contribution $\Psi^{(1)}_{\mathrm{I}}$ is not treated here since its result is well-known, at least as far as it accounts for weak pair correlation.

Neglecting consequently $\Psi^{(1)}_{\mathrm{II}}$ and $\Psi^{(1)}_{\mathrm{I}}$ the eigenfunction up to first order follows from Eqs. (36), (37) and (44) to be

$$\begin{aligned}\Psi=\Psi^{(0)}_{\mathrm{I}}\prod^{l}\Bigg[\Phi_{\nu_l}(\boldsymbol{\xi}_l)-\frac{e^2}{r_0}\,\langle\nu_l\,|\,\xi\,|\,\nu_l+1\rangle\,\frac{1}{x_{\nu_l}}\,\Phi_{\nu_l+1}(\boldsymbol{\xi}_l)\\ +\sum_s\sum_i\left\{\frac{e\,e_i}{\Delta\varepsilon_{\nu_l}}\int\Phi^*_{\nu_{is}}(\boldsymbol{\xi}_s-\Delta\boldsymbol{r})\,\Phi_{\nu_l}(\boldsymbol{\xi}_l)\left[\frac{1}{\Delta\boldsymbol{r}}-\frac{1}{\Delta\boldsymbol{r}+\boldsymbol{\xi}_l}\right]\mathrm{d}\boldsymbol{\xi}_l\right\}\Phi_{\nu_{is}}(\boldsymbol{\xi}_i)\end{aligned} \tag{45}$$

where $x_{\nu l}$ is $\Delta\varepsilon_{\nu l}$ or kT depending on whether $\Delta\varepsilon_{\nu l}$ is larger or smaller than $k\,T$.

So far we have not taken into account degeneracy. This is done by replacing throughout Eq. (45) 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 $\widetilde{\Phi}_\nu$. Then due to the resonance degeneracy the zero order eigenfunction is composed of terms of the form[21]

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[20] Y. N. Ryabinin, Gases at High Densities and Temperatures, Pergamon Press, London 1961.

[21] The quasi-static treatment of the exchange degeneracy effects is justified within the range of our condition (28).

$$\Psi_{l,i}^{(0)} = c_l\,\tilde{\Phi}_\nu(\boldsymbol{\xi}_l) + c_i\,\tilde{\Phi}_\nu(\boldsymbol{\xi}_i) \tag{46}$$

where c_l and c_i are given by

$$c_l = \left\{\frac{V_{li}}{2\,|V_{li}|}\left[1 \pm \frac{V_{ll}-V_{ii}}{\sqrt{(V_{ll}-V_{ii})^2+4\,|V_{li}|^2}}\right]\right\}^{1/2}, \tag{47}$$

$$c_i = \pm\left\{\frac{V_{li}}{2\,|V_{li}|}\left[1 \mp \frac{V_{ll}-V_{ii}}{\sqrt{(V_{ll}-V_{ii})^2+4\,|V_{li}|^2}}\right]\right\}^{1/2} \tag{48}$$

with

$$V_{ll} = e^2 \int \tilde{\Phi}_\nu^*(\boldsymbol{\xi}_l)\,\tilde{\Phi}_\nu(\boldsymbol{\xi}_l)\,\frac{1}{|\boldsymbol{\xi}_l+\boldsymbol{R}_l-\boldsymbol{r}_i|}\,\mathrm{d}\boldsymbol{\xi}_l, \tag{49}$$

$$V_{ii} = e^2 \int \tilde{\Phi}_\nu^*(\boldsymbol{\xi}_i)\,\tilde{\Phi}_\nu(\boldsymbol{\xi}_i)\,\frac{1}{\xi_i}\,\mathrm{d}\boldsymbol{\xi}_i \tag{50}$$

$$V_{li} = e^2 \int \tilde{\Phi}_\nu^*(\boldsymbol{\xi}_l)\,\tilde{\Phi}_\nu(\boldsymbol{\xi}_l+\boldsymbol{R}_l-\boldsymbol{r}_i) \cdot \frac{1}{|\boldsymbol{\xi}_l+\boldsymbol{R}_l-\boldsymbol{r}_i|}\,\mathrm{d}\boldsymbol{\xi}_l. \tag{51}$$

Using the definition of free and bound from page 2013 we see from Eq. (46) that the demarcation ε_b between free and bound should be put where $c_l \cong c_i$ holds. According to Eqs. (47), (48) this is true if the relation

$$|(V_{ll}-V_{ii})| \ll 4\,|V_{li}| \tag{52}$$

is fulfilled.

It follows trivially from our free-bound concept that the eigenfunction of all states above the demarcation ε_b given through Eq. (52) are non-hydrogen-like. Therefore $\varepsilon_\mathrm{h} = \varepsilon_\mathrm{b}$ holds provided that the limit for ε_h prescribed by Eq. (37) is not more restrictive. Eq. (37) defines the principal quantum number of ε_h by

$$(e^2/r_0{}^2)\,\langle n_h\,|\,\xi\,|\,n_h\rangle = k\,T \tag{53}$$

since it is readily shown that in the range below the critical density $\Delta\varepsilon < k\,T$ always holds.

Classical Approximation to the Partition Function of the Free Particles

The investigaitons in the preceding chapter answer the questions I and II on page 2014. We now turn to treat question III regarding the possibility of a classical approximation to the partition function of the free particles.

The quantum-mechanical partition function is given by

$$Q = t\,r\,\exp\{-\beta\,\mathbf{H}\} \tag{54}$$

where $\mathbf{H}$ is the matrix of the HAMILTON operator of our system and $\beta = (k\,T)^{-1}$.

We now group all those states of the system together which contain the same number of free particle states and designate these groups by the index (s). Accordingly we subdivide the trace in Eq. (54) resulting in

$$Q = \sum_s Q_s = \sum_s (t\,r\,\exp\{-\beta\,\mathbf{H}\})_s\,. \tag{55}$$

Here each term of the sum belongs to a fixed subdivision in free and bound states. In the following it is sufficient to study one of these terms.

If we neglect the interaction between the above defined groups of free and bound particles[22] the HAMILTON operator $\hat{H}$ is separable into two independent parts $\hat{H}_\mathrm{f}$ and $\hat{H}_\mathrm{b}$. Under these circumstances Q can be factorized in the form

$$Q = Q_\mathrm{f}\,Q_\mathrm{b} = t\,r\,\exp\{-\beta\,\mathbf{H}_\mathrm{f}\}\cdot t\,r\,\exp\{-\beta\,\mathbf{H}_\mathrm{b}\}\,. \tag{56}$$

Applying the eigenfunctions of H_b in the calculation of Q_b we arrive at

$$Q_\mathrm{b} = \frac{1}{N_\mathrm{b}!}\left[(2\,\pi\,M\,k\,T/h^2)^{3/2}\,\sum_n \exp\{-\beta\,\varepsilon_n\}\right]^{N_\mathrm{b}} \tag{57}$$

where N_b is the number of bound states, ε_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

$$Q_\mathrm{f} = \frac{1}{(N_\mathrm{f}!)^2\,h^{6N_\mathrm{f}}} \int_{\Gamma_\mathrm{f}} \exp\{-(i/\hbar)\,\Sigma\,\boldsymbol{p}_i\,\boldsymbol{r}_i\} \cdot \exp\{-\beta\,\hat{H}_\mathrm{f}\} \cdot \exp\{(i/\hbar)\,\Sigma\,\boldsymbol{p}_i\,\boldsymbol{r}_i\}\,\mathrm{d}\boldsymbol{p}\,\mathrm{d}\boldsymbol{r} \tag{58}$$

where Γ_f is the volume of the phase space occupied by all free states and N_f the number of free electrons. The term $(N_\mathrm{f}!)^2$ is due to the exchange degeneracy. In principle this phenomenon produces additional off-diagonal terms in (58), which are small as follows from the results in the investigations[23–25, 14].

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[22] 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.

[23] J. G. KIRKWOOD, Phys. Rev. **44**, 31 [1933].

[24] E. WIGNER, Phys. Rev. **40**, 749 [1932].

[25] H. S. GREEN, J. Chem. Phys. **19**, 955 [1951].

Aiming to calculate the function

$$u = \exp\{-\beta \hat{H}_{\mathrm{f}}\} \cdot \exp\{(i/\hbar) \, \Sigma \, \boldsymbol{p}_i \boldsymbol{r}_i\} \\ = \exp\{-\beta \hat{H}_{\mathrm{f}}\} \, \zeta \qquad (59)$$

we want to solve Bloch's equation

$$\hat{H}_{\mathrm{f}} \, u + \frac{\partial u}{\partial \beta} = 0 \qquad (60)$$

through the Ansatz

$$u = w \, e^{-\beta H} \zeta \qquad (61)$$

where H is the classical Hamilton function.

For w follows the differential equation

$$-\frac{\hbar^2}{2} \sum_i \frac{\Delta_i}{m_i} \{\zeta \, w \, e^{-\beta V}\} - w \, \zeta \, E_{\mathrm{kin}} \, e^{-\beta V} + \zeta \, e^{-\beta V} \frac{\partial w}{\partial \beta} \\ = 0 \qquad (62)$$

where V is the potential energy of the free particles.

Eq. (62) may be simplified to

$$\frac{\partial w}{\partial \beta} - e^{\beta V} \Big[i \hbar \sum_i \frac{\boldsymbol{p}_i}{m_i} \nabla_i (e^{-\beta V} w) \\ + \frac{\hbar^2}{2} \sum_i \frac{\Delta_i}{m_i} (e^{-\beta V} w) \Big] = 0 \qquad (63)$$

using

$$\frac{-\hbar^2}{2} \sum_i \frac{\Delta_i \, \zeta}{m_i} = \sum_i \frac{p_i^2}{2 \, m_i} \zeta \approx E_{\mathrm{kin}} \, \zeta \, . \qquad (64)$$

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

With the boundary condition

$$\lim_{\beta \to \infty} w = 1 \qquad (65)$$

Eq. (63) is readily transformed into the integral equation

$$w = 1 + i \hbar \int_0^\beta e^{Vt} \Big\{ \sum_i \frac{\boldsymbol{p}_i}{m_i} \nabla_i (e^{-Vt} w) \ \mathrm{d}t \\ + \int_0^\beta \frac{\hbar^2}{2} e^{Vt} \Big\{ \sum_i \frac{\Delta_i}{m_i} (e^{-Vt} w) \Big\} \mathrm{d}t \, . \qquad (66)$$

If we look for solutions of the form

$$w = \sum_{k=0}^{\infty} \hbar^k \, w_k \qquad (67)$$

iteration produces the recursion formula

$$w_0 = 1 \, , \qquad w_1 = -\frac{i \, \beta^2}{2} \sum_i \frac{\boldsymbol{p}_i}{m_i} \nabla_i V \, , \qquad (68)$$

$$w_k = \int_0^\beta e^{Vt} \Big[\tfrac{1}{2} \sum_i \frac{\Delta_i}{m_i} (e^{-Vt} w_{k-2}) \\ + i \sum \frac{\boldsymbol{p}_i}{m_i} \nabla_i (e^{-Vt} w_{k-1}) \Big] \mathrm{d}t \, .$$

Therefore Q_{f} is given by

$$Q_{\mathrm{f}} = \int_{\Gamma_{\mathrm{f}}} e^{-\beta H} \sum_i \hbar^k \, w_k \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{p} \, . \qquad (69)$$

In principle the derivation of this result follows a procedure developed by Kirkwood [23].

To decide on the possibilities of a classical approximation to the partition function (69) we consider the integrand in the two ranges $r^2 \gtrless r_{\mathrm{w}} \, \lambda$.

For $r^2 > r_{\mathrm{w}} \, \lambda$ the condition

$$\left| \sum_i \frac{\hbar^2}{12 \, (k \, T)^2} \left[\frac{e_i \, e_j}{m_i} \delta(r_{ij}) - \frac{1}{2 \, k \, T} \left(\frac{e_i \, e_j}{r_{ij}^2} \right)^2 \right] \right| \ll 1 \qquad (70)$$

is fulfilled and the integrand may be approximated by

$$e^{-\beta V} \sum_{k=0}^{\infty} \hbar^k \, w_k = e^{-\beta V} \, . \qquad (71)$$

For $r^2 < \lambda \, r_{\mathrm{w}}$ the development (67) 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 $V \cong V_{ij} = e_i \cdot e_j / r_{ij}$. Under these circumstances their contribution w_{ij} to w may be factorized and is given by

$$\frac{\partial w_{ij}}{\partial \beta} - e^{\beta V_{ij}} \Big\{ i \, h \Big[\Big(\frac{\boldsymbol{P}}{M} \nabla_R + \frac{\boldsymbol{p} \nabla}{\mu} \Big) w_{ij} \, e^{-\beta V_{ij}} \Big] \\ + \frac{\hbar^2}{2} \Big[\Big(\frac{\Delta_R}{M} + \frac{\Delta}{\mu} \Big) w_{ij} \, e^{-\beta V_{ij}} \Big] \Big\} = 0 \qquad (72)$$

where we have introduced relative $(\boldsymbol{r}, \boldsymbol{p})$ and center of gravity $(\boldsymbol{R}, \boldsymbol{P})$ coordinates and momenta. With the Ansatz

$$w_{ij} = \exp\{(2 \, i/\hbar) \, \boldsymbol{P} \, \boldsymbol{R}\} \, \omega(r) \, \exp\{+\beta (e_i \, e_j / r)\} \, , \\ r = r_{ij} \, . \qquad (73)$$

$\omega(r)$ is defined by the equation

$$(\hbar^2 / 2 \, \mu) \, \Delta \omega + (i \, \hbar / \mu) \, \boldsymbol{p} \, \nabla \, \omega - e_i \, e_j \, \omega / r = 0. \\ (74)$$

As is readily proven by substitution the solution of Eq. (74) for small values of r can be represented by the development

$$\omega = \sum (A_s \, r^s + B_s / r^{s+1}) \, \mathcal{P}_s \qquad (75)$$

where $\mathcal{P}_s$ 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 $A \cong 1$ and $B \cong 0$ so that we finally have

$$w_{ij} \approx \exp\{(2 \, i/\hbar) \, \boldsymbol{P} \, \boldsymbol{R}\} \exp\{+\beta \, e_i \, e_j / r\} \, . \qquad (76)$$

In view of the results (61) and (76) we claim that the classical partition function

$$Q_{\mathrm{fc}} = \prod_{i=+,-} \left(\frac{2\,\pi\, m_i\, k\, T}{h^2}\right)^{3\,N_{\mathrm{f}}/2} \frac{1}{(N_{\mathrm{f}}!)^2} \int e^{-\beta V}\, \mathrm{d}\boldsymbol{r} \qquad (77)$$

is applicable provided that the integration over the Γ-space is limited to interparticle distances $r^2 > r_{\mathrm{w}}\,\lambda$.

Our claim is correct if the following two relations hold:

For pairs of oppositely charged particles

$$\frac{\int\limits_0^{c r_0} \int\limits_{p_{\min}}^{\infty} \exp\left\{-\beta\left(\frac{p^2}{2\,\mu} - \frac{e^2}{r}\right)\right\}\, \Omega_O\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{p}}{\int\limits_{(\lambda r_{\mathrm{w}})^{1/2}}^{c r_0} \int\limits_0^{\infty} \exp\left\{-\beta\left(\frac{p^2}{2\,\mu} - \frac{e^2}{r}\right)\right\} \mathrm{d}\boldsymbol{p}\, \mathrm{d}\boldsymbol{r}} = 1 - \frac{\int\limits_{(\lambda r_{\mathrm{w}})^{1/2}}^{c r_0} \int\limits_0^{p_{\min}} \exp\left\{-\beta\left(\frac{p^2}{2\,\mu} - \frac{e^2}{r}\right)\right\} \mathrm{d}\boldsymbol{p}\, \mathrm{d}\boldsymbol{r}}{\int\limits_{(\lambda r_{\mathrm{w}})^{1/2}}^{c r_0} \int\limits_0^{\infty} \exp\left\{-\beta\left(\frac{p^2}{2\,\mu} - \frac{e^2}{r}\right)\right\} \mathrm{d}\boldsymbol{p}\, \mathrm{d}\boldsymbol{r}} = 1 - \varkappa_0 \approx 1 \qquad (78)$$

For pairs of equally charged particles

$$\frac{\int\limits_0^{c r_0} \exp\{-\beta\, e^2/r\}\ \Omega_{\mathrm{e}}\, \mathrm{d}\boldsymbol{r}}{\int\limits_{(\lambda r_{\mathrm{w}})^{1/2}}^{c r_0} \exp\{-\beta\, e^2/r\}\ \mathrm{d}\boldsymbol{r}} = 1 - \frac{\int\limits_0^{(\lambda r_{\mathrm{w}})^{1/2}} \mathrm{d}\boldsymbol{r}}{\int\limits_{(\lambda r_{\mathrm{w}})^{1/2}}^{c r_0} \exp\{-\beta\, e^2/r\}\ \mathrm{d}\boldsymbol{r}} = 1 - \varkappa_0 \approx 1 \qquad (79)$$

where according to Eq. (76) Ω is given by

$$\Omega^{\mathrm{o}}_{\mathrm{e}} = \begin{cases} \exp\{\mp\beta\, e^2/r\} & \text{for} \quad r < (\lambda\, r_{\mathrm{w}})^{1/2} \\ 1 & \text{for} \quad r > (\lambda\, r_{\mathrm{w}})^{1/2} \end{cases}, \qquad (80)$$

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

To evaluate Eqs. (78) and (79) we employ the transformations

$$y = r_{\mathrm{w}}/r\,, \qquad x = p/\sqrt{2\,\pi\,\mu\, k\, T}\,, \; \varepsilon = r_{\mathrm{w}}/c\, r_0\,. \qquad (81)$$

The limitation $p > p_{\min}$ in Eq. (78) is due to the fact that the free particles can have only energy states above the limit given in Eq. (52) and with the transformations (81) this limitation reads

$$x^2 \geqq y - \varepsilon\,. \qquad (82)$$

Using Eqs. (81) and (82) in Eqs. (78) and (79) we find

$$\varkappa_0 = \frac{4}{\sqrt{\pi}} \frac{\int\limits_{\varepsilon}^{1} e^y \{ \int\limits_0^{\sqrt{y-\varepsilon}} e^{-x^2} x^2\, \mathrm{d}x \} y^{-4}\, \mathrm{d}y}{\int\limits_{\varepsilon}^{1} e^y\, y^{-4}\, \mathrm{d}y} \qquad (83)$$

and

$$\varkappa_{\mathrm{e}} = \frac{\int\limits_0^{\varepsilon} (e^{-y} - 1)\ y^{-4}\, \mathrm{d}y}{\int\limits_{\varepsilon}^{1} e^y\, y^{-4}\, \mathrm{d}y}\,. \qquad (84)$$

Evaluation of these integrals results in

$$\varkappa_0 = \frac{10^{-2}}{c^{3/2}} \left(\frac{\lambda}{r_{\mathrm{w}}}\right)^{3/2} \cdot \frac{1}{N_{\mathrm{D}}}\,, \quad \varkappa_{\mathrm{e}} \approx \varkappa_0{}^2 \qquad (85)$$

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 $\lambda \gg r_{\mathrm{w}}$ holds. These corrections are due to additional contributions from the range $r_{\mathrm{w}} < r < \sqrt{r_{\mathrm{w}}\,\lambda}$ and exchange degeneracy effects for distances below λ.

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. (52) shows that the energy ε_{b} characterizing the "free-bound-limit" is roughly determined by

$$\varepsilon_{\mathrm{b}} \approx -e^2/r_0\,. \qquad (86)$$

II. The introduction of a discontinuous limit for "hydrogenlike behaviour" suffers from inherent uncertainties similar to those mentioned in the previous section. The definition of this limit classifies all states as "non-hydrogenlike" for which the perturbation is of the same order of magnitude as the zero order hydrogen function. Since it is readily shown tha the value for ε_{h} following from Eq. (53) is smaller than ε_{b} we have

$$\varepsilon_{\mathrm{h}} \cong \varepsilon_{\mathrm{b}} \cong -e^2/r_0\,. \qquad (87)$$

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 representing the free states can be described quasi-classically by the classical canonical partition function with the exclusion of interparticle distances $r^2 < \lambda r_w$. The factor representing the bound states has to be described quantum-mechanically with the energy limitation given in Eq. (86).

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 μ-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 Γ-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. (86).

Shift and broadening. As we 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. (87)] is different from the INGLIS–TELLER limit [10]. The reasons are that near $\varepsilon_h = \varepsilon_b$ the static approach underlying the INGLIS–TELLER is not valid and exchange degeneracy effects prevail.

Our investigation gives no energy shift for the low and 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 $r^2 < \lambda r_w$ 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 tacitly 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 ($\lambda > r_w$).