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Equilibrium Theory of a Partially Ionized Plasma*

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A detailed study is made of the use of the Debye potential as the effective interaction between the electron and proton of a hydrogen atom in a partially ionized plasma. The chemical potentials of the constituents are calculated and examined in the light of the requirement that they be consistent with a single free-energy function. On this basis a Saha equation is derived which is consistent and correct up to terms of the order of the Debye-Hückel energy. It is further shown that the next order, obtained by expanding the effective potential in powers of the Bohr radius divided by the Debye length, is incorrect.

I. INTRODUCTION

This paper is concerned with the equilibrium composition of a partially ionized plasma. For simplicity we confine our attention to a system consisting only of hydrogen atoms and equal numbers of electrons and protons. To obtain an equation of state for N_A, the number of atoms (which for a closed system determines the numbers of electrons, N_e, and of protons N_p), one evaluates the partition function as a function of the number of atoms. The equilibrium equation (a generalized Saha equation) is then obtained by maximizing the phase volume as a function of N_A.

The classical difficulty in this procedure, which was recognized very early in the history of this problem, is that the partition function of an isolated hydrogen atom is divergent. The divergence is due to the neglect of the interaction of the hydrogen atom with its surroundings. Many different methods have been used to overcome this difficulty. The volume available for the atomic wave function can be limited by various physical assumptions[1–6] which lead to a finite number of atomic energy levels and a convergent partition function. The particular assumption used, of course, depends upon the physical conditions of the plasma.

Here we will deal with a plasma at temperatures and densities such that it is in a "partially ionized state." Specifically the temperature is in a range wherein essentially all of the atoms are in the ground state, and the density of atoms is low enough so that we can neglect the atom-atom interactions. Under these conditions it seems physically attractive to use the Debye potential as the effective interaction between the electron and proton of a hydrogen atom. This is justified by arguments based upon the plasma shielding of the Coulomb interaction. Since for a Debye potential there are a finite number of bound states, this approach automatically yields a convergent atomic partition function. Historically, this method was suggested by Ecker and Weizel,[7] and, more recently, has been used frequently for detailed calculations in partially ionized plasmas.[8,9]

The use of the Debye potential implies that one is treating the plasma according to the Debye-Hückel theory, which is a systematic approximation scheme ordered by the small parameter $\beta e^2\kappa$, where $\beta = 1/kT$ and κ is the inverse Debye length, $(4\pi\beta e^2 N/V)^{1/2}$. There are two principal questions which we consider here with regard to the use of the Debye potential for the effective interaction in the atomic hamiltonian. The first question concerns the terms of order $\beta e^2\kappa$, and the second, higher-order corrections.

There has been disagreement as to whether the effective potential should be[7]

$$V_{\mathrm{eff}}^{(1)} = -e^2(e^{-\kappa r}/r) - e^2\kappa \tag{1}$$

or[8,9]

$$V_{\mathrm{eff}}^{(2)} = -e^2 e^{-\kappa r}/r \, . \tag{2}$$

The second form, Eq. (2), results in energy eigenvalues shifted to the first order by the constant value $e^2\kappa$. This results in versions of the generalized Saha equation which differ in the coefficient of the $\beta e^2\kappa$ term, thus giving different values for the so-called lowering of the ionization potential. The higher-order terms may be obtained by calculating the atomic partition function using energy eigenvalues obtained with the shielded Debye potential.

Here we shall systematically examine both the lowering of the ionization-potential term and the significance of the higher-order corrections. By following a procedure which starts from first principles of quantum statistical mechanics, we are able to avoid the ambiguities associated with *ad hoc* methods. Results will be obtained upon the introduction of suitable physical approximations. These approximations, however, will be made in the context of a systematic derivation. The procedure to be used will be to derive the equilibrium Saha equation by evaluating the quantum partition function in a classical limit for a fixed number of atoms (and free electrons and protons) and then obtaining the number of atoms which corresponds to the maximum volume in phase space.

This, of course, is the same as minimizing the free energy as a function of N_A, or equating chemical potentials, i.e.,

$$\mu_A = \mu_e + \mu_p, \tag{3}$$

where the subscripts A, e, and p indicate that the chemical potential is that of an atom, electron or proton, respectively.

We calculate the chemical potentials of the different constituents by a generalization of a method developed by the present authors in a previous publication.[10] This method, the distribution-of-potential method, is particularly suited to this problem, because the chemical potentials are obtained directly for a constituent in terms of the probability distribution function of its interaction potential with the other constituents of the system. By calculating separately the chemical potentials, the results can be subjected to an independent check in that these chemical potentials should be derivable in a particular order of approximation from a unique free-energy function.

In Sec. II we will review the distribution-of-potential method and discuss the extension required for an application to this problem. Section III contains a derivation of the chemical potential of an atom based upon a quantum-mechanical generalization of the distribution-of-potential method. A calculation of the chemical potential of an electron is presented in Sec. IV. In Sec. V we will discuss the compatibility of the results for the chemical potentials with respect to the requirement that they be derivable from a unique free-energy function. On this basis the best approximate form of the Saha equation will be obtained. These considerations will also be used to discuss both of the questions mentioned previously which have led to controversies in the literature[11–14]; that is, the questions of the lowering of the ionization-potential terms ($\beta e^2\kappa$ terms) and the atomic partition-function correction terms (higher-order terms).

The principal conclusions are:

1. The effective potential to be used for the interaction of the proton and electron in the hydrogen atom which is correct to order $\beta e^2\kappa$ is,

$$V_{\text{eff}}^{(1)} = -e^2 e^{-\kappa r}/r - e^2\kappa\,,$$

the shifted Debye potential.

2. The higher-order "corrections" obtained with the use of $V_{\text{eff}}^{(1)}$ are incorrect. Indeed, in view of the results for the electron and proton chemical potentials presented in Sec. IV, it will become apparent that higher-order corrections can only be obtained by taking into account the details of the quantum-mechanical atom-electron and atom-proton interactions. A consequence of this result is that there does not appear to be any justification for basing quantitative conclusions for a partially ionized plasma on the details of calculations of the bound states of the Debye potential.

II. METHOD

Here we will review the distribution-of-potential method as it was previously derived and applied to classical single-component fluids. If the particles interact via a two-body potential $u(\vec{r})$, we define the potential at a point to be

$$\varphi(\vec{r}) = \sum_{j=1}^{n} u(\vec{r} - \vec{r}_j), \tag{4}$$

where N is the number of particles in the fluid. Regarding $\varphi(\vec{r})$ as a random variable whose statistics are determined by the equilibrium distribution, we are able to write the chemical potential in terms of $P(\varphi)$, the probability distribution function of the potential. We suppress the dependence of φ on $\vec{r}$ because (neglecting points near the surface) for a homogeneous fluid $P(\varphi)$ is not a function of position. The result, which is proved rigorously in Ref. 10, is

$$\beta\mu = \ln(\lambda^3 N/V) - \ln\int P(\varphi)e^{-\beta\varphi}d\varphi. \tag{5}$$

Here V is the volume and λ is the thermal De Broglie wavelength, $h/(2\pi mkT)^{1/2}$. We may gain insight into the meaning of Eq. (5) by the following non-rigorous argument. We write the partition function of the system in the following form,

$$e^{-\beta F_N} = \frac{1}{N!\lambda^{3N}}\int d\vec{r}_2 \cdots \int d\vec{r}_N$$
$$\times \exp\{-\beta[u_{23}(\vec{r}_{23}) + \cdots + u_{N-1,N}(\vec{r}_{N-1,N})]\}$$
$$\times \int d\vec{r}_1 \exp\{-\beta[u_{12}(\vec{r}_{12}) + \cdots + u_{1N}(\vec{r}_{1N})]\}, \tag{6}$$

where F_N is the free energy of the N-particle system. The integral over the coordinates of particle 1 is of course still a function of all the other coordinates of the fluid. However for typical distributions of the coordinates, $\vec{r}_2, \ldots, \vec{r}_N$, in performing the integral over $\vec{r}_1$, the values which the exponent assumes will be determined by the probability distribution of φ. In other words for "typical" $\vec{r}_2 \ldots \vec{r}_N$ one has

$$\int d\vec{r}_1 \exp\{-\beta[u_{12}(\vec{r}_{12}) + \cdots + u_{1N}(\vec{r}_{1N})]\}$$
$$\simeq V\langle e^{-\beta\varphi}\rangle. \tag{7}$$

Thus we obtain

$$e^{-\beta F_N} = \frac{V}{\lambda^3 N}\,\frac{\langle e^{-\beta\varphi}\rangle}{(N-1)!\lambda^{3(N-1)}}\int d\vec{r}_2 \cdots \int d\vec{r}_N$$
$$\times \exp\{-\beta[u_{23}(\vec{r}_{23}) + \cdots + u_{N-1,N}(\vec{r}_{N-1,N})]\},$$

or

$$e^{-\beta(F_N - F_{N-1})} = \frac{V}{\lambda^3 N}\langle e^{-\beta\varphi}\rangle. \tag{8}$$

As $F_N - F_{N-1}$ approaches $\partial F/\partial N = \mu$ in the limit as N approaches infinity, we directly obtain Eq. (5). Equation (3) has been applied to a hard sphere gas,[10] and, with the necessary extensions, to a fully ionized plasma.[15] The problem of calculating the chemical potential 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 chemical potentials of the constituents of a partially ionized plasma, it is necessary to obtain a suitable quantum-mechanical generalization of Eq. (5). One can then write expressions for μ_A and μ_e in terms of the statistics of their interactions with the constituents of the partially ionized plasma. The 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. However, for the conditions in which we are interested, the charged component (plasma) and the atoms are weakly coupled, and the relevant commutators that appear in quantum statistical-mechanical perturbation procedures are expected to be small. In this approximation the leading terms in the expressions for the chemical potentials will be shown to be the suitable generalizations of Eq. (5).

III. THE CHEMICAL POTENTIAL OF AN ATOM

To derive the quantum-mechanical generalization of Eq. (5) for the chemical potential of a hydrogen atom in a system of electrons, protons, and atoms, we write the quantum partition function corresponding to that part of phase space containing N_A atoms and N_c charged particles (consisting of equal numbers of unbound electrons and protons),

$$Z(N_A, N_c) = \mathrm{Tr}\rho^{N_A, N_c}, \quad \text{where} \quad \rho^{N_A, N_c} = e^{-\beta H(N_A, N_c)} \tag{9}$$

is the density matrix for the system of N_A atoms and N_c charged particles, and $H(N_A, N_c)$ is the corresponding Hamiltonian. The Hamiltonian can be written,

$$H(N_A, N_c) = \sum_{j=1}^{N_A}(\mathcal{H}_j + K_j^A) + \sum_{\lambda=1}^{N_c}(K_\lambda^c + \sum_{\lambda \neq \lambda'}^{N_c} V_{\lambda\lambda'}^{cc}) + \sum_{j=1}^{N_A}\sum_{\lambda=1}^{N_c} V_{j,\lambda}^{Ac}, \tag{10}$$

where $\mathcal{H}_j + K_j^A$ is the unperturbed atomic Hamiltonian and the center-of-mass kinetic energy operator for the jth atom,

$$K_\lambda^c + \sum_{\lambda' \neq \lambda}^{N_c} V_{\lambda\lambda'}^{cc}$$

is the kinetic energy operator and the operator for the potential energy of interaction with all other charged particles for the λth charged particle, and $V_{j\lambda}^{Ac}$ is the potential energy operator for the interaction of atom j and charged particle λ. Note that the atom-atom interaction has been neglected in Eq. (10). This is appropriate for systems containing a sufficiently dilute atomic component (i.e., the degree of ionization is moderately high).

The partition function of the above system with one more atom added is

$$Z(N_A + 1, N_c) = \mathrm{Tr}\,\rho^{N_A + 1, N_c} = \mathrm{Tr}\exp\{-\beta[H(N_A, N_c) + \mathcal{H}_a + \textstyle\sum_\lambda V_{a\lambda}^{Ac} + K_a]\}, \tag{11}$$

where $\mathcal{H}_a + K_a^A$ is the Hamiltonian of the extra atom and $V_{a\lambda}^{Ac}$ is the interaction energy of the extra atom with the λth charged particle. It can be written explicitly as

$$V_{a\lambda} = ee_\lambda/|r_a^+ - r_\lambda| - ee_\lambda/|r_a^- - r_\lambda|, \tag{12}$$

where r_a^+ and r_a^- are the coordinates of the proton and electron of the extra atom.

If we assume that the atom is weakly coupled to the plasma we can neglect all commutators involving $V_{a\lambda}$ in an S-matrix type expansion of the operator $\rho^{N_A + 1, N_c}$ so that,

$$\rho^{N_A + 1, N_c} \approx \exp[-\beta(\mathcal{H}_a + K_a^A + \textstyle\sum_\lambda V_{a\lambda})]\rho^{N_A, N_c}. \tag{13}$$

Equation (13) is exact only in the case when $V_{a\lambda}$ is zero. However, the approximation involved should be good at temperatures such that only the lower atomic levels are significantly occupied. This is because the atom-plasma coupling is strong only for highly excited atomic states. The approximation Eq. (13) is a common assumption in theories of spectral line shapes[16] which reproduce experimental data to within a few percent.

In the context of the weak coupling approximation Eq. (13), the partition function of the system with the extra atom, can be written in the form,

$$\begin{aligned} Z(N_A + 1, N_c) = (N_A + 1)^{-1}\mathrm{Tr}_c \int d\varphi^+ \int d\varphi^- \, \mathrm{Tr}_a \exp[-\beta(K_a + \mathcal{H}_a + \varphi^+ + \varphi^-)] \\ \times \mathrm{Tr}_A \rho^{N_A, N_c} \delta(\varphi^+ - \textstyle\sum_\lambda e_\lambda/|r_a^+ - r_\lambda|)\delta(\varphi^- + \textstyle\sum_\lambda e_\lambda/|r_a^- - r_\lambda|), \end{aligned} \tag{14}$$

where φ^+ and φ^- are scalar variables of integration. The use of delta functions in Eq. (14) implies that the weak coupling approximation has been made again, as $\sum_\lambda V_{a\lambda}{}^{Ac}$ has been commuted with $H(N_A, N_c)$. In the same approximation, the trace operation in Eq. (14) has been factored so that Tr_c, Tr_A, and Tr_a are independent traces over the N_c charged particle coordinates, the N_A atomic coordinates, and the extra atom, respectively. The factor $(N_A + 1)^{-1}$ has been included to account for the indistinguishability of the extra atom, i. e., the trace over the atomic coordinates must be performed with properly antisymmetrized functions.

The probability distribution function of the positions of the charged particles is defined as

$$P(r_1, \cdots, r_{N_c}) = \mathrm{Tr}_A \rho^{N_A, N_c} / Z(N_A, N_c). \tag{15}$$

Introducing the distribution function of the potential at two points (in this case, the positions of the ion and electron of the atom),

$$P(\varphi^+, \varphi^-) = \mathrm{Tr}_c \left[\delta\left(\varphi^+ - \sum_{\lambda=1}^{N_c} \frac{e_\lambda}{|r^+ - r_\lambda|}\right) \delta\left(\varphi^- + \sum_{\lambda=1}^{N_c} \frac{e_\lambda}{|r^- - r_\lambda|}\right) P(r_1, \cdots, r_{N_c}) \right], \tag{16}$$

Eq. (14) can now be written as

$$Z(N_A + 1, N_c)/Z(N_A, N_c) = (N_A + 1)^{-1} \mathrm{Tr}_a \int d\varphi^+ \int d\varphi^- \, P(\varphi^+, \varphi^-) \exp[-\beta(K_a + \mathcal{H}_a + \varphi^+ + \varphi^-)], \tag{17}$$

where the definition of φ^+ and φ^- may be obtained from Eq. (12). The integrand in Eq. (17) is independent of the center-of-mass coordinate of the atom. Taking the trace over the center-of-mass coordinates and momenta we obtain in the thermodynamic limit, $N_A \to \infty$, $V \to \infty$, $N_A/V \to \mathrm{const}$, the atomic chemical potential,

$$\mu_A \approx kT \ln(\lambda_A{}^3 N_A/V) - kT \ln \mathrm{Tr}_a \exp(-\beta \mathcal{H}_a{}^{\mathrm{eff}}), \tag{18}$$

where Tr_a is a trace only over the atomic bound states; and, in the weak coupling approximation, $\mathcal{H}_a{}^{\mathrm{eff}}$ is defined as

$$\exp(-\beta \mathcal{H}_a{}^{\mathrm{eff}}) = \int d\varphi^+ \int d\varphi^- \, P(\varphi^+, \varphi^-) \exp[-\beta(\mathcal{H}_a + \varphi^+ + \varphi^-)]. \tag{19}$$

Equation (18) is the quantum generalization of Eq. (5) which was sought for the calculation of the chemical potential of the atomic component. In Ref. 15 it has been shown that, in the Debye-Hückel approximation,

$$P(\varphi^+, \varphi^-) = [2\pi\kappa kT(1 - \sigma^2)]^{-1/2} \exp\{-[(\varphi^+)^2 + (\varphi^-)^2 - 2\sigma\varphi^+\varphi^-]/2\kappa kT(1 - \sigma^2)\}, \tag{20}$$

with $\quad \sigma = (1 - e^{-\kappa r})/\kappa r, \quad$ and $\kappa = (4\pi\beta e^2 N_c/V)^{1/2}$,

where κ is the inverse Debye length. Substituting this in Eq. (19) and performing the integration, we obtain

$$\exp(-\beta \mathcal{H}_a{}^{\mathrm{eff}}) = \exp(-\beta \mathcal{H}_a) \exp\{-\beta[(e^2/r)(1 - e^{-\kappa r}/r) - e^2\kappa]\}, \tag{19$'$}$$

which is, again in the weak coupling approximation,

$$\exp(-\beta \mathcal{H}_a{}^{\mathrm{eff}}) = \exp\{-\beta[-(\hbar^2/2m)\nabla_a{}^2 - e^2 e^{-\kappa r}/r - e^2\kappa]\}, \tag{21}$$

in agreement with the hypothesis of Ecker and Weizel.[7] Substituting this expression in Eq. (18) we obtain the chemical potential of an atom in a partially ionized plasma

$$\mu_A = kT \ln(\lambda_A{}^3 N_A/V) - kT \ln \sum_n e^{-\beta E_n{}^*}, \tag{22}$$

where $E_n{}^*$ are the energy levels (finite in number) of an electron in the shifted Debye-Hückel potential, $-e^2 e^{-\kappa r}/r - e^2\kappa$. At temperatures such that only the ground state of the hydrogen atom is significantly occupied, Eq. (22) becomes,

$$\mu_A \cong kT \ln(\lambda_A{}^3 N_A/V) - |E_0| - e^2\kappa^2 a_B + \cdots, \tag{23}$$

where a_B is the Bohr radius, and $|E_0|$ is the hydrogenic ionization potential, 13.6 eV. The correction term, the last term in Eq. (23), is calculated by expanding the effective potential, and is of higher order than the Debye-Hückel theory approximation (which is ordered by the parameter $\beta e^2\kappa$), since $\kappa a_B \ll 1$. It will be shown in Sec. V that no significance can be attached to this term.

IV. THE CHEMICAL POTENTIAL OF AN ELECTRON

The chemical potential of the electron is calculated to the first order from the classical formula, Eq. (5). The interaction potentials for an electron may be decomposed into a sum of the potential due to the atoms, φ_A and the charged particles, φ_c, i.e.,

$$\varphi = \varphi_c + \varphi_A . \tag{25}$$

As the plasma-atom coupling is weak, we assume that the φ_A and φ_c are statistically independent and we write $P(\varphi)$, the distribution function of φ in terms of the $P_1(\varphi_A)$ and $P_2(\varphi_c)$ distribution functions of φ_A and φ_c, respectively,

$$P(\varphi) = \int d\varphi_c \int d\varphi_A \delta(\varphi - \varphi_c - \varphi_A) P_1(\varphi_A) P_2(\varphi_c). \tag{26}$$

Inserting Eq. (22) into Eq. (5), the result is

$$\beta\mu_e = \ln(\lambda_e^3 N_e/V) - \ln \int d\varphi_A e^{-\beta\varphi_A} P(\varphi_A) - \ln \int d\varphi_c e^{-\beta\varphi_c} P(\varphi_c). \tag{27}$$

The last term in Eq. (27) corresponds to the contribution to the chemical potential of an electron in a fully ionized plasma. This integral has been calculated in Ref. 15 and, in the Debye-Hückel approximation, results in the well-known expression,

$$\ln \int d\varphi_c e^{-\beta\varphi_c} P(\varphi_c) = \tfrac{1}{2}\beta e^2 \kappa . \tag{28}$$

Since the atoms are assumed to be non-interacting, $P(\varphi_A)$ in the second term of Eq. (23) can be assumed to be generated by a random distribution of atoms. Thus this term can be written

$$\int d\varphi_A P(\varphi_A) e^{-\beta\varphi_A} \cong V^{-1} \int dr_c \exp[-\beta \textstyle\sum_a u_{ca}(r_c - r_a)] \equiv I, \tag{29}$$

where r_c represents an integration over the coordinates of a single charged particle. To obtain Eq. (25) we have assumed that an integration of $P(\varphi_A)e^{-\beta\varphi_A}$ over the random variable φ_A is equivalent to integrating $\exp[-\beta\sum_a u(r - r_a)]$ over the space of the charged particle. This is valid only when the atomic density is sufficiently low so that there is no significant overlap of the interactions between the charged particle and the atoms in the system. In other words we calculate the first virial associated with the electron-atom interaction. We can now write Eq. (25) in the form

$$I \approx 1 + (N_A/V) \int dr_c (e^{-\beta u_{ca}(r_c - r_a)} - 1), \tag{30}$$

and hence Eq. (23) becomes

$$\beta\mu_e = \ln(\lambda_c^3 N_c/V) - \tfrac{1}{2}\beta e^2 \kappa - \ln\left\{1 + \frac{N_A}{V} \int dr_c (e^{-\beta u_{ca}(r_c - r_a)} - 1)\right\}. \tag{31}$$

To evaluate the last term correctly one must know the correct quantum mechanical interaction between an atom and the electron. In lieu of this, one can use the results of detailed quantum-mechanical calculations of electron-hydrogen atom scattering. For this purpose, we need only use the corresponding quantum-mechanical expression.[17] We thus write

$$I \approx 1 + (\lambda_e^3 N_A/V) \times \mathrm{Tr}(\exp\{-\beta H_0 + u_{ca}(r_c - r_a)\} - \exp\{-\beta H_0\}). \tag{32}$$

Following the procedure of Ref. 18, the radial eigenstates, which are Bessel functions, are normalized in a sphere of radius R. This implies the boundary condition

$$k^l(n_u)R - \tfrac{1}{2}l\pi + \delta_l(k) = n_u \pi \tag{33}$$

for the eigenstates of the Hamiltonian $H_0 + u(r_c - r_a)$, and

$$k^l(n_0)R - \tfrac{1}{2}l\pi = n_0 \pi \tag{34}$$

for the eigenstates of H_0. In the above equation, $k^l(n)$ is the asymptotic momentum of the nth eigenstate and $\delta_l(k)$ is the phase shift of the lth partial wave. We assume that the temperature is such that $\delta_l(k)$ is nonzero only for s wave ($l = 0$) scattering. Thus in performing the trace in Eq. (32) we may transform the sum over states to an integral over momentum and obtain

$$\mathrm{Tr}(e^{-\beta[H_0 + u_{ca}(r_c - r_a)]} - e^{-\beta H_0}) = \int e^{-\beta\hbar^2 k^2} \left(\frac{dn_u}{dk} - \frac{dn_0}{dk}\right) dk, \tag{35}$$

where dn/dk can be obtained from Eqs. (33) and (34), i.e.,

$$\frac{dn_u}{dk} - \frac{dn_0}{dk} = \frac{1}{\pi} \frac{d\delta_0(k)}{dk} . \tag{36}$$

Thus far we have neglected spin. If we take this into account by writing δ_0^T and δ_0^S for the phase shift in triplet and singlet spin states, we can now write Eq. (31) as

$$\beta\mu_e = \ln(\lambda_e^3 N_e/V) - \tfrac{1}{2}\beta e^2 \kappa - \ln\left[1 + \frac{\lambda_e^3 N_A}{V} \int dk e^{-\beta\hbar^2 k^2/2m} \times \frac{1}{4\pi}\left(3\frac{d\delta_0^T(k)}{dk} + \frac{d\delta_0^S(k)}{dk}\right)\right]. \tag{37}$$

The phase shifts for electron-atom s-wave scattering have been calculated,[19] and in the energy range of interest are approximately given by

$$\delta_0{}^T = \tfrac{1}{2}\pi - ka^T, \quad \delta_0{}^S = \tfrac{1}{2}\pi - ka^S, \tag{38}$$

where the best values of the constants are, $a^T = 1.91a_B$, $a^S = 6.22a_B$ (a_B is the Bohr radius). With these values we have

$$\beta\mu_e = -\ln(\lambda_e{}^3N_e/V) - \tfrac{1}{2}\beta e^2\kappa + \tfrac{3}{4}(N_A/N_e)(\kappa a_B)^2 + \cdots . \tag{39}$$

The chemical potential of the proton can be calculated in a completely analogous manner. The phase shifts for proton-atom s-wave scattering have also been calculated.[20] The resulting expression for μ_p will differ from Eq. (39) only in the coefficient of the third term on the right-hand side.

V. DISCUSSION

In this section we will review the results of the preceding sections for the chemical potentials of the constituents, and discuss them in consideration of the fact that they must be derivable from a single free energy function. That is they must satisfy the integrability conditions

$$\frac{\partial\mu_A}{\partial N_e} = \frac{\partial\mu_e}{\partial N_A}; \quad \frac{\partial\mu_A}{\partial N_p} = \frac{\partial\mu_p}{\partial N_A}; \quad \frac{\partial\mu_e}{\partial N_p} = \frac{\partial\mu_p}{\partial N_e}. \tag{40}$$

The chemical potentials calculated in the preceding two sections are

$$\beta\mu_A \approx \ln(\lambda_A{}^3N_A/V) - \beta|E_0| - \kappa a_B\beta e^2\kappa + \cdots \tag{41a}$$

$$\approx \ln(\lambda_A{}^3N_A/V) - \beta|E_0| - 4\pi e^4\beta^2 a_B(N_p+N_e)/V + \cdots \tag{41b}$$

and

$$\beta\mu_e \approx \ln(\lambda_e{}^3N_e/V) - \tfrac{1}{2}\beta e^2\kappa + \tfrac{3}{4}(N_A/N_e)(a_B/\beta e^2)^2(\beta e^2\kappa)^2 + \cdots \tag{42a}$$

$$\approx \ln(\lambda_e{}^3N_e/V) - \tfrac{1}{2}\beta e^2[4\pi\beta e^2(N_e+N_p)/V]^{1/2} + 6\pi\beta e^2 a_B{}^2(N_A/V). \tag{42b}$$

For each of the chemical potentials we have written the first line in a form which exhibits the ordering of the terms in powers of the small parameter, $\beta e^2\kappa$. In the second form we have written the terms in the notation which displays the functional dependence on N_A, N_p, and N_e. As stated at the end of Sec. IV, the chemical potential of the proton will have the same form as μ_e with a different numerical coefficient for the third term.

We note that there is no difficulty with the consistency conditions up to terms of order $\beta e^2\kappa$, as the Debye-Hückel term, which involves the number of charged particles, appears only in μ_e (and μ_p). Up to terms of first order in the Debye-Hückel theory, it is therefore correct to write, the free energy in the form,

$$\beta F^{\mathrm{DH}} = \beta F_0 - \beta|E_0|N_A - \tfrac{1}{3}(N_e+N_p)\beta e^2\kappa, \tag{43}$$

where F_0 is the free energy of non-interacting ideal gases of N_p protons, N_e electrons and N_A atoms. The consistency condition provides a further confirmation of the necessity for the shift $-e^2\kappa$ in the effective potential, for if there were not such a term, there would be an additional term of order $\beta e^2\kappa$ in Eqs. (41). This would have to arise from a term $N_A\beta e^2\kappa$ in the free energy, which is inconsistent with the results obtained for the chemical potential of the electrons.

With regard to the higher-order terms in the chemical potentials [the third terms on the right-hand side of both Eqs. (41) and (42)] it is immediately apparent that they are inconsistent. Although both of these terms may be thought of as being due to interactions between atoms and charged particles, they differ in their functional dependence on the temperature. It should be recalled that in deriving Eq. (41) for μ_A, commutators were neglected, and there is no reason to believe that the terms neglected are smaller than those obtained in the expansion of the effective potential. On the other hand, the third term in Eq. (42) is the leading term in the electron-atom interaction and should be correct in its functional dependence. We therefore conclude that the third term in Eqs. (42) is the correct one, and the one in Eqs. (41) is wrong. Accordingly, the free energy of a partially ionized plasma taking the plasma-atom interaction into account to the first order is

$$\beta F = \beta F^{\mathrm{DH}} + cN_A(N_e+N_p)/VkT, \tag{44}$$

where c is a constant.

From Eqs. (42), one may see that the last term is of order $(\beta e^2\kappa)^2$. If, however, one wishes to include all terms to that order one should also include the higher-order terms in the free energy of a plasma.[21, 22] The second term in Eq. (44), however, is apparently the leading term involving intercomponent interactions.

To summarize, the above remarks have the following implication in the calculation of μ_A. The use of a shielded Debye potential to obtain corrections to the chemical potential (or partition function) of an atom in a low atomic state is not justified. That is, the quantum corrections which are neglected in the derivation of the atomic Hamiltonian, containing the shielded potential, are of the same order as the corrections due to the shielded potential. We can make no statement about corrections to higher atomic levels, since the weak coupling approximation utilized in Sec. III is incorrect for these levels. **On the basis of** the theory presented here, which is valid only when the temperature is low enough so that only the low atomic states are significantly populated, the lower atomic energy levels should be calculated with the ordinary hydrogen Hamiltonian (the small $|\vec{r}_+ - \vec{r}_-|$ limit of $\mathcal{H}^{\text{eff}}$).

With this understanding we may use the chemical potentials, Eqs. (42) and (43), to write the Saha equation for hydrogen which is consistent to first order in the Debye-Hückel approximation as,

$$\frac{N_e N_p}{N_A} = \frac{V}{h^3}\left(\frac{2\pi m_p m_e}{m_p + m_e}\right)^{3/2} \frac{e^{-\beta e^2 \kappa}}{e^{-\beta|E_0|}} . \qquad (45)$$

This Saha equation agrees with the corrected version of the Ecker-Weizel theory[7] obtained by Duclos and Cambel,[12] but differs from the expression obtained by Harris.[8]

Since our calculations are valid only for the low atomic states, where the weak coupling approximation holds, we cannot comment on the problem of the divergence of the hydrogen-atom partition function. However, the use of the Debye potential to obtain a convergent expression has been shown, at least in the "partially ionized state" considered here, to be inconsistent. From this it would appear that a satisfactory resolution of the divergence problem must await a more complete understanding of the quantum mechanical many-body problem.

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