

## LEVEL SHIFT AND NEGATIVE ION DISINTEGRATION IN A PLASMA

G. A. KOBZEV

Institute of High Temperatures, USSR Academy of Sciences

Submitted January 6, 1971

Zh. Eksp. Teor. Fiz. 61, 582-592 (August, 1971)

The effect of the surrounding charged particles on negative ions in a plasma is investigated. The Stark level shift of a negative ion in a plasma and effects due to lowering of the negative ion potential barrier by the microfields of the nearest charged particles are considered. The level shift is studied by quantum field theory methods. The mass and vertex operator diagrams are analyzed. An expression is derived for the shift; it is negative and leads to growth of the binding energy. The behavior of negative ions in electric microfields is considered on the basis of model concepts. A correction for the ion concentration, to allow for the disintegration due to the microfields, is obtained. Estimates are made for realistic experimental conditions. It is shown that recent experiments on nitrogen and air plasma radiation can be explained if allowance is made for the disintegration. The result for the shift of the photodetachment threshold of J, which is determined by the energy-level shift and by the lowering of the potential barrier, agrees with the experimental data.

## 1. INTRODUCTION

THE concentration  $n_-$  of the negative ions (NI) in a certain state is usually calculated from the formula for ideal gases:

$$n_- = n_a n_e (g_- / \Sigma_a) (h^2 / 2\pi m k T)^{3/2} \exp(A / kT), \quad (1)$$

where  $n_a$  and  $n_e$  are respectively the concentrations of the neutral atoms and of the electrons,  $T$  is the temperature,  $A$  is the energy of electron detachment from the NI (the electron affinity of the atom),  $\Sigma_a$  is the partition function of the atom, and  $g_-$  is the statistical weight of an isolated NI in the state under consideration.

The interaction of the particles in plasmas of intermediate and high density may exert a noticeable influence on the degree of ionization and other thermodynamic properties of the plasma, and on its optical and transport properties. The influence of particle-interaction effects in the plasma on the NI concentration was considered in<sup>[1-4]</sup>. In<sup>[1,2]</sup>, a thermodynamic calculation was performed to determine the Coulomb interaction of charged particles in the plasma and it was shown that the "Debye" correction to the detachment potential vanishes in the calculation of the NI concentration. The lowering of the potential barrier for the electron in the NI under the influence of the plasma microfields was considered in<sup>[13]</sup>, where suitable corrections to formula (1) were proposed. The contribution made to the free energy by the interaction of the atoms and charged particles, and the corresponding correction to the NI detachment potential, were calculated in<sup>[4]</sup>, but the value of this correction is in practice always small compared with the effects considered in<sup>[3]</sup> and in the present article.

The main factors influencing the NI concentration in the plasma are the change of the energy of electron detachment from the NI and the change of the effective statistical weight of the NI in the plasma, due to the microfields of the plasma. The detachment energy of the NI in the plasma changes primarily because of the lowering of the potential barrier and because of the

Stark shift of the level. The change of the NI detachment energy can become manifest also in the NI absorption spectrum in the form of a shift of the photodetachment threshold.

## 2. ENERGY LEVEL SHIFT OF NEGATIVE ION

The shift of the levels of single-electron atoms and positive ions in a plasma was investigated in<sup>[5,6]</sup> by quantum field-theory methods. The atom was described by a two-particle electron-ion temperature Green's function, the poles of which give the energy spectrum of the atom in the plasma, and the pole shift of which determines the width (imaginary part) and the shift (real part) of the energy levels.

The low-temperature ( $kT/Ry \ll 1$ ) plasma under consideration constitutes a Boltzmann gas in thermodynamic equilibrium with a temperature  $T = \beta^{-1}$ , and consists of electrons, ions, and atoms of one kind. The following interactions take place: Coulomb for the pairs electron-electron  $U_{ee}$ , ion-ion  $U_{ii}$ , and ion-electron  $U_{ie}$ , electron-atom interaction  $U_{ea}$ , and ion-atom interaction  $U_{ia}$ . We neglect the atom-atom interaction. The concrete form of  $U_{ea}$  and  $U_{ia}$  will be specified subsequently. We describe the negative ion by a two-particle electron-atom Green's function  $G_{ea}$ . The method of constructing this function and methods of solving the resultant equations are analogous to those of<sup>[5,6]</sup>. The difference lies in the choice of the most important diagrams and in the wave functions.

Equation for the paired Green's function. The integral equation for the temperature Green's function  $G_{ea}$  is

$$(G_e^{-1} G_a^{-1} + V_{ea}) G_{ea} = 1, \quad (2)$$

where  $G_e$  and  $G_a$  are the single-particle electron and atomic Green's function, and  $V_{ea}$  is the compact vertex part for the electron-atom interaction. We substitute in (2) the expressions for  $G_e$  and  $G_a$  (the Dyson equation):

$$G_e^{-1} = S_e^{-1} - M_e, \quad G_a^{-1} = S_a^{-1} - M_a, \quad (3)$$

where  $S_e(S_a)$  is the single-particle Green's function of the noninteracting electrons (atoms):

$$\begin{aligned} S_e^{-1}(p, \omega_p) &= i\omega_p - p^2/2m + \mu_e; \\ S_a^{-1}(K, \omega_a) &= i\omega_a - K^2/2M + \mu_a, \end{aligned} \quad (4)$$

$M_e(M_a)$  are the mass operators of the electrons (atoms), describing the action of the plasma on the electron (atom), and  $\mu_e(\mu_a)$  is the chemical potential of the electrons (atoms).

We represent the vertex operator in the form

$$V_{ea} = U_{ea} + V_{ea}^1, \quad (5)$$

where  $U_{ea}$  is of zero order in the density and the  $V_{ea}^1$  are of higher orders. We have the following equation for the zeroes of  $G_{ea}^{-1}$ :

$$(S_e^{-1}S_a^{-1} + U_{ea} + W)\Psi = 0. \quad (6)$$

The perturbation operator is of the form

$$W = -S_e^{-1}M_a - M_eS_a^{-1} + M_eM_a + V_{ea}^1. \quad (7)$$

The function  $\Psi$  is connected with the paired Green's function in analogy with the connection between the wave function and the Green's function of the Schrödinger equation.  $W$  tends to zero when the density tends to zero. We solve the equation by perturbation theory. The method for integrating an equation of the type (2) or (6) was considered in<sup>[7]</sup> for the case of quantum electrodynamics and has been expanded to include quantum statistics in<sup>[5,6]</sup>. The first-order perturbation-theory correction to the energy is<sup>[6]</sup>

$$\Delta E = \beta^{-1} \sum_p \int d^3p \bar{\Psi}(p) W \Psi(p), \quad (8)$$

where the function  $\Psi$  is connected with the wave function  $\varphi(p)$  of the relative motion of the electron and of the core by the relation

$$\Psi(p, K) = -S_e(vK + p)S_a(vK - p)(i\omega_a + \mu - T(p))\varphi(p). \quad (9)$$

This expression is written in the c.m.s. of the electron-atom system,  $K$  is the momentum of the mass center,  $P$  is the momentum of relative motion,  $\mu = \mu_e + \mu_a$ ,  $T(p) = K^2/2M + p^2/2m$ .

**Mass and vertex operators.** Let us consider the quantities that enter in the perturbation operator  $W$ , namely the electron and atom mass operators  $M_e$  and  $M_a$ , and the vertex part  $V_{ea}^1$ .

The electron mass operator describes in our problem the influence of the plasma on the bound electron. The following types of interaction should be taken into account: electron-free atom  $U_{ea}$ , electron-free electron  $U_{ee}$ , and electron-positive ion  $U_{ei}$ . We introduce the following graphic symbols: a thin line for the electrons, a thick line for the ions, a double thin line for atoms, a wavy line for a Coulomb interaction, and a dashed line for the interaction between an atom and a charged particle. Diagrams 1–7 of Fig. 1 are the first- and second-order diagrams for the electron mass operator.

Each of the first-order diagrams of the electron mass operator, 1 and 4, in which the Coulomb-interaction line as a zero momentum, diverges, but by virtue of the quasineutrality of the plasma as a whole, these diagrams cancel each other. The same pertains also to the second-order diagrams 3 and 6, each of which

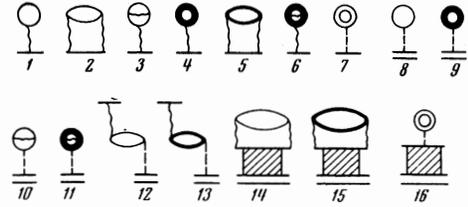


FIG. 1

has one Coulomb-interaction line with zero momentum transfer. Each of the second-order diagrams of the type 2 and 5 diverges at small momentum transfers  $q$ , i.e., at large distances, like  $q^{-1}$ . To eliminate this divergence at large distances it is necessary to take the Debye screening into account. The divergence of the diagrams 2 and 5 is eliminated by replacing one Coulomb potential  $u(k) = 4\pi e^2/k^2$  by the effective potential, which at  $\omega_k = 0$  goes over into the Debye potential

$$\bar{u}(k) = 4\pi e^2 / (k^2 + \kappa^2), \quad \kappa^2 = -4\pi e^2 \beta (n_e + n_i). \quad (10)$$

The sum of the diagrams 2 and 5 makes the following contribution to  $M_e$ :

$$M_{2,5}(p) = \frac{n_i + n_e}{(2\pi)^3} \sum_q \int d^3q u(q) \bar{u}(q) S_e(p+q). \quad (11)$$

Let us consider the contribution made to the electronic mass operator by the interaction with the atoms. The atom-discharge interaction will be considered in the "gas" approximation, assuming that the effective radius of the forces is much smaller than the average distance between the interacting particles. In this approximation it suffices to take into account only the diagrams of first order in the atom-charge interaction. The contribution of diagram 7 to the electron mass operator is

$$M_7(p) = U_{ea}(0) n_a / (2\pi)^3 \beta. \quad (12)$$

Here  $U_{ea}(q)$  is the Fourier transform of the electron-atom interaction potential.

Let us consider the atomic mass operator, which takes into account the action of the plasma particles on the atom. We are interested in the interaction of the atom (the core of the negative ion) with the charged plasma particles. The diagrams for the atomic mass operator are numbered 8–11.

The first-order diagrams 8 and 9 with zero momentum transfer have identical sign and their sum yields

$$M_{8,9}(p) = (n_i + n_e) U_{ea}(0) / (2\pi)^3 \beta. \quad (13)$$

Diagram 10 corresponds to the expression

$$M_{10}(p) = \frac{U_{ea}(0)}{(2\pi)^6 \beta^2} \sum_{p_1, \omega_q} \int d^3p_1 d^3q \bar{u}(q) S_e^2(p_1 - q) S_e(p). \quad (14)$$

Diagram 11 corresponds to an expression similar to (14) with the index  $e$  replaced by  $i$ . Diagrams 12 and 13 of the vertex part give the effective potential  $\bar{U}_{ea}(k)$ :

$$\bar{U}_{ea}(k) = U_{ea}(k) [\Pi_e(k, \omega_k) + \Pi_i(k, \omega_k)] \bar{u}(k). \quad (15)$$

**Calculation of shift.** The energy-level shift is determined by the real part of expression (8). The formu-

las obtained above for the mass operators and the vertex part make it possible to calculate the shift. The expression for the shift due to diagrams 2 and 5 coincides, apart from a factor, with the contribution from the analogous diagrams 1 and 2 in<sup>[6]</sup>, and is of the form

$$\Delta E_{2,5} = -\sqrt{(n_i + n_e)kT} 2\sqrt{\pi} e^3 \int d^3p \frac{|\varphi(\mathbf{p})|^2}{p^2/2m - E}. \quad (16)$$

Here  $E < 0$ ,  $i\omega_K + \mu - T(\mathbf{p}) = E - p^2/2m$ . The integral in (16) is positive, so that the shift is  $\Delta E_{2,5} < 0$ , i.e., towards a higher value of the binding energy<sup>1)</sup>.

Let us examine the contributions of the other diagrams to the shift. For an estimate, we use the polarization potential for both electrons and ions:

$$U_{ea}(r) = -ae^2 / (r^2 + r_0^2)^2. \quad (17)$$

The Fourier transform of (17) is

$$U_{ea}(q) = -\frac{ae^2\pi^2}{r_0} e^{-qr_0}. \quad (18)$$

At  $q = 0$  we have  $U_{ea}(0) = -ae^2\pi^2/r_0$ , so that the diagrams with  $U_{ea}(0)$  make finite contributions. The effective potential  $\bar{U}_{ea}(k)$ , defined by formula (15), will then take the form

$$\bar{U}_{ea}(q) = \beta(n_i + n_e) \frac{4\pi^3\alpha e^4}{r_0} \frac{e^{-qr_0}}{q^2 + \kappa^2}. \quad (19)$$

Estimating the contributions of diagrams 8–13, we compare them with  $\Delta E_{2,5}$ . We write down the results without proof:

$$\Delta E_{8,9} = \gamma_1 \Delta E_{2,5}, \quad \gamma_1 = \frac{kT}{Ry} \frac{\alpha}{64\pi^2 r_0} \frac{a_0}{d}; \quad (20)$$

$$\Delta E_{12,13} = \gamma_2 \Delta E_{2,5}, \quad \gamma_2 = \frac{\alpha}{\sqrt{\pi} r_0^2} \frac{a_0}{d}. \quad (21)$$

Here  $\alpha$  and  $r_0$  are in atomic units, and  $d$  is the Debye radius. The values of  $\gamma_1$  and  $\gamma_2$  in our case of low-temperature Debye plasma are much smaller than unity.

The contribution of diagrams 10 and 11 differs from  $\Delta E_{2,5}$  by a factor proportional to  $(a_0/d)^2$ , and is negligibly small.

For the contribution from diagram 7 we have

$$\Delta E_7 = -Ry n_e a_0^3 kT I \frac{\alpha}{4\pi r_0}. \quad (22)$$

Of all the diagrams containing atom–charge interaction lines, this is the most important one.

Diagrams 14, 15, and 16 with ladder potential (shaded square) describe the change of the NI energy as a result of its interaction as a whole with charges (14, 15) or neutrals (16). In the calculation of the change of the NI detachment potential, the contribution of the diagrams 14 and 15 is offset by an exactly equal Debye decrease due to the interaction of the free elec-

trons with the charges. The contribution of diagram 16 is proportional to  $n_a\alpha/r_0$  and is offset, in the calculation of the change of NI detachment potential, by an equal contribution from the interaction of the free electrons with the atoms<sup>2)</sup>.

Thus, the level shift of the NI energy as a result of the interaction with the charges is determined by the diagrams 2 and 5, and the shift due to the interaction with the atoms is determined by diagram 7:

$$\Delta E = \Delta E_{2,5} + \Delta E_7, \quad (23)$$

or

$$\frac{\Delta E}{Ry} = -kTI \left[ (n_e + n_i)^{1/2} a_0^{3/2} \left( \frac{Ry}{kT} \right)^{1/2} 4\sqrt{2\pi} + n_e a_0^3 \frac{\alpha}{4\pi r_0} \right], \quad (23a)$$

$$I = \int d^3p \frac{|\varphi(\mathbf{p})|^2}{p^2/2m + |A|} \quad (24)$$

The second term in the square brackets of (23a) (the contribution from the interaction with the atoms) exceeds the first term (the contribution from the interaction with the charges) provided

$$n_e / n_a \lesssim 2.5 \cdot 10^{-3} n_a T \alpha^2 r_0^{-2} (T \text{ in } 10^4 \text{ }^\circ\text{K}). \quad (25)$$

In the calculation of the mass and vertex operators and of the matrix elements of these operators, it was assumed that the plasma is weakly nonideal with respect to the Coulomb interaction, i.e., of the Debye type, and is rarefied with the respect to the atom–charge interaction, i.e., the ‘‘gas’’ approximation is valid. The first of these conditions imposes the following limitation on the concentration of the charged particles:

$$n_e \ll 10^{19} \cdot T^3 (T \text{ in } 10^4 \text{ }^\circ\text{K}). \quad (26)$$

The second condition imposes a limitation on the concentration of the atoms:

$$n_a \ll 2 \cdot 10^{24} (r_0 / \alpha)^3. \quad (27)$$

Let us estimate the integral (24) which enters in the expression for the level shift. The radial wave functions of the outer s-electron in the NI is taken in asymptotic form<sup>[9]</sup>:

$$R(r) = \frac{f\sqrt{A}}{\pi\sqrt{r}} K_{l+1/2}(\sqrt{A}r),$$

where  $K_{l+1/2}$  is a MacDonald function,  $A$  is the binding energy in Rydberg units, and  $f$  is a constant determined by the behavior of the bound wave function near the core. For an NI with an external p-electron we use the analytic Hartree-Fock wave functions<sup>[10]</sup>. Changing over to the momentum representation, we obtain after integration in (24) particularly for the s-electron,

$$I = f^2 / 32\pi^2 A. \quad (28)$$

It follows from this expression that the level shift should be largest for NI with small binding energy  $A$ .

The use of perturbation theory for the determination of  $\Delta E$  leads to the requirement  $\Delta E/A \ll 1$ . The shift due to the interaction with the charge satisfies

<sup>2)</sup>The ionization potential of the atom is decreased as a result of the interaction of the atom with the charges by an amount proportional to  $n_a\alpha/r_0$ . This result was obtained by Timan [8].

<sup>1)</sup>In the case of the atom, the core is a positive ion and a contribution of the same magnitude as from diagrams 2 and 5, but of opposite sign, is made by diagrams of the same type for the ion mass operator and by diagrams of the type 12 and 13 for the vertex operator. The result is [5,6]

$$\Delta E = -(z^2 - 1)^2 kT e^2 \kappa \int d^3p \frac{|\varphi(\mathbf{p})|^2}{p^2/2m - E}$$

and is equal to zero for the atom ( $z = 1$ ); for a positive ion, just as in our case,  $\Delta E < 0$ .

this inequality provided (for an NI with an outer  $s$ -electron)

$$n_e \ll 4 \cdot 10^{24} A^4 f^{-4} T^{-1} \quad (A \text{ in eV}, T \text{ in } 10^4 \text{ }^\circ\text{K}). \quad (29)$$

The smallness of the shift due to the interaction with the atoms, in comparison with the binding energy, imposes the following condition (for an NI with outer  $s$ -electron)

$$n_a \ll 3 \cdot 10^{27} A^2 r_0 T^{-1} \alpha^{-1} \quad (A \text{ in eV}, T \text{ in } 10^4 \text{ }^\circ\text{K}). \quad (30)$$

Conditions (29) and (30) are, as a rule, much less stringent than (25) and (27).

The matrix elements of the mass and vertex operators, contained in the expression for the shift, have been calculated at zero values of  $\omega_k$  and in the limit of small  $k$ . This corresponds to allowance for only small momentum transfers, i.e., for perturbing particles passing at long range. The contribution of perturbing particles passing at close range to the Stark shift can be estimated as follows. A constant electric field produces in non-hydrogen-like atoms, and particularly in NI, a quadratic Stark effect

$$\Delta E(\epsilon) = -\alpha \epsilon^2, \quad (31)$$

where  $\alpha$  is the polarizability of the NI and  $\epsilon$  is the field intensity. Assuming that the electric field produced by the close positive ion to be quasistationary, we can estimate the shift due to ions passing at close range, substituting in (31) the most probable value of the microfield intensity. Estimates show that the shift determined by formula (31) is much smaller than (23). Electrons passing at close range make a still smaller contribution to the shift than (30), since the microfield produced by them is rapidly alternating and a retardation effect takes place<sup>[11]</sup>.

Thus, the level shift of the NI in the plasma is determined by interaction with remote perturbing particles and has a negative sign.

### 3. LOWERING OF POTENTIAL BARRIER AND DISINTEGRATION OF NI IN PLASMA

NI in homogeneous electric field. The potential energy of the outer electron, at sufficiently large values of the electron coordinate, are written in this case in the form

$$V(r_e) = -ae^2 / 2r_e^4 - e\epsilon r_e,$$

where  $\alpha$  is the polarizability of the atom and  $\epsilon$  the field intensity. The lowering of the potential barrier in the field direction is therefore

$$\Delta U(\epsilon) = \frac{2}{3} \alpha \epsilon (2ae / \epsilon)^{3/2}. \quad (32)$$

For a certain critical field intensity  $\epsilon_{cr}$ , the value of  $\Delta E$  reaches the value of the affinity energy  $A$  (height of the potential barrier).  $\epsilon_{cr}$  is given by the expression

$$\epsilon_{cr} = \frac{2}{3} A^{2/3} e^{-1} (\frac{2}{3} ae^2)^{-1/2}. \quad (33)$$

It is obvious that  $\epsilon_{cr}$  determined in (33) is the upper limit at which all the NI are already disintegrated. At field intensities smaller than  $\epsilon_{cr}$  by a factor of 2, a considerable fraction of the NI disintegrate in the electric field. An estimate of  $\epsilon_{cr}$  in accordance with

formula (33) gives, for example, for the NI  $\text{He}^-$ , a value  $\sim 500$  kV/cm. Disintegration of weakly-bound  $\text{He}^-$  in a constant electric field was observed in experiments<sup>[12,13]</sup>. The field intensity at which a considerable fraction of the NI disintegrated was 200 kV/cm. At an intensity 400–600 kV/cm, all the NI turned out to be disintegrated. A quantum-mechanical theory of the decay of NI in a constant electric field at intensities  $\epsilon \ll \epsilon_{cr}$  is considered in<sup>[9]</sup>. Without performing exact calculations with allowance for the three-dimensional character of the system and for the subbarrier transitions, we confine ourselves to introduction of a correction factor  $a$ , which apparently assumes values between 1 and  $\frac{1}{2}$ . We assume that

$$\epsilon_{cr} \approx a^{2/3} A^{2/3} e^{-1} (\frac{2}{3} ae^2)^{-1/2}. \quad (33a)$$

NI in the microfield of the plasma. An estimate based on the data of<sup>[14]</sup> shows that the most probable value of the electric microfield intensity reaches, at a negatively charged point of the plasma, a value 20–40 kV/cm at an electron concentration  $n_e = 10^{16}$   $\text{cm}^{-3}$  and 400–800 kV/cm at  $n_e = 10^{18}$   $\text{cm}^{-3}$ . At such values of the electric field intensity, the weakly-coupled NI can apparently be disintegrated, and not only because of the tunnel transitions, but also, and this is of particular importance for the calculation of thermodynamic quantities, as a result of classical ionization, and the ionization equilibrium can become displaced in this case.

The electric microfields produced by the positive ions can be regarded as quasistationary. To this end it is necessary that the characteristic lifetime of the ionic microfield  $t_M = r_{cr} / v_T$  ( $r_{cr} = \sqrt{\epsilon_{cr} r_e}$ ;  $v_T = \sqrt{6kT/M}$ , where  $M$  is the ion mass and  $T$  the temperature) be much larger than the period of revolution  $\tau_e = 2\pi r_0 / v_e$  of the electron on its orbit in the NI ( $r_0$  is of the order of one to several Bohr radii;  $v_e$  is the velocity of the bound electron in the NI, of the order of  $8\pi f^{-1} \sqrt{A/M}$  for the  $s$  state of the NI, where  $f$  was defined earlier and  $m$  is the electron mass). In fact,

$$\delta = \frac{\tau_e}{t_M} \approx \sqrt{\frac{m}{M}} \left( \frac{A}{Ry} \right)^{1/2} \left( \frac{kT}{Ry} \right)^{1/2} \alpha^{-1/2} \ll 1.$$

For the NI  $\text{N}^-$ , for example, an estimate yields  $\delta \approx 0.1 \sqrt{m/M} \ll 1$ .

Thus, the field of an ion passing by at a distance  $r_{cr}$  is quasistatic. The lowering  $\Delta \bar{U}$  of the potential barrier of the NI in the plasma due to the nearest ions can be calculated by averaging (32) over the distribution of the ionic microfield  $f(\epsilon)$ :

$$\Delta \bar{U} = \int_0^{\epsilon_{cr}} \Delta U(\epsilon) f(\epsilon) d\epsilon / \int_0^{\epsilon_{cr}} f(\epsilon) d\epsilon. \quad (34)$$

The value of  $\epsilon_{cr}$  is determined below.

The microfields produced by the nearest electrons vary in time at rates close to the velocity of the bound electrons in the NI, and therefore do not produce an effective lowering of the barrier.

NI concentration in the plasma. If the value of the ionic microfield  $\epsilon$  exceeds  $\epsilon_{cr}$ , then the NI should disintegrate, and at lower values of  $\epsilon$ , owing to the lowering of the barrier, the binding energy decreases in comparison with the value possessed by the NI

without allowance for the microfields of the nearest ions, i.e., in comparison with  $A + |\Delta E|$ , where  $\Delta E$  is defined in (26). The concentration of NI located in a given microfield  $\epsilon < \epsilon_{cr}$  is determined by formula (1), in which the binding energy is given by  $A + \Delta E - \Delta U(\epsilon)$ . The concentration of the NI in a field  $\epsilon > \epsilon_{cr}$  is equal to zero. The total NI concentration is determined by integrating over the entire microfield distribution. The expression obtained in this case differs from (1) by a factor

$$\int_0^{\epsilon_{cr}} \exp \left[ \frac{\Delta E - \Delta U(\epsilon)}{kT} \right] f(\epsilon) d\epsilon = \xi_1 \xi_2. \quad (35)$$

$\epsilon_{cr}'$  is determined from (33a), in which the binding energy is replaced by  $A + |\Delta E|$ , and the distribution of the microfields  $f(\epsilon)$  is normalized by the condition  $\int_0^{\infty} f(\epsilon) d\epsilon = 1$ . Expression (35) can be represented as a product of two factors:

$$\xi_1 = \int_0^{\epsilon_{cr}'} f(\epsilon) d\epsilon, \quad (36)$$

$$\xi_2 = \int_0^{\epsilon_{cr}'} \exp \left[ \frac{\Delta E - \Delta U(\epsilon)}{kT} \right] f(\epsilon) d\epsilon / \int_0^{\epsilon_{cr}'} f(\epsilon) d\epsilon. \quad (37)$$

The factor  $\xi_1$  has the meaning of the effective decrease of the statistical weight, while  $\xi_2$  takes into account the average change of the binding energy for the realized ions. Usually  $\xi_2 \cong 1$ . We therefore confine ourselves to a consideration of  $\xi_1$ , putting  $\xi_2 = 1$ , which is in accord with the accuracy with which these quantities are determined.

To determine  $\xi_1$  we used the function  $f(\epsilon)$  obtained by extrapolating, with respect to the charge, the data of [14] for the ionic microfield at positively-charged and neutral points. The distribution function obtained in this manner is shown in Fig. 2. For large values of

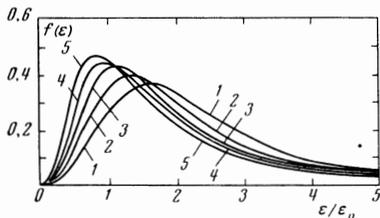


FIG. 2. Distribution function of microfield at a negatively charged point for a number of values of the parameter  $a_1 = \bar{r}/d$ . Curve 1— $a_1 = 0$ , 2—0.2, 3—0.4, 4—0.6, 5—0.8,  $\epsilon_0 = e/\bar{r}^2$ .

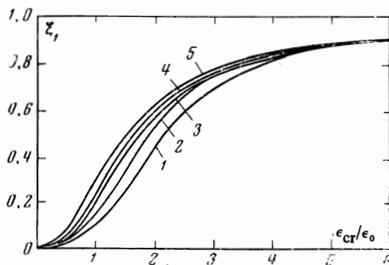


FIG. 3. Dependence of the factor  $\xi_1$  on the critical field intensity for a number of values of the parameter  $a_1 = \bar{r}/d$ . Curve 1— $a_1 = 0$ , 2—0.2, 3—0.4, 4—0.6, 5—0.8,  $\epsilon_0 = e/\bar{r}^2$ .

$\epsilon$ , we used the function in the nearest-neighbor approximation. Using the distribution functions obtained in this manner, we obtained the dependence of the factor  $\xi_1$  on  $\epsilon_{cr}$ . It is shown in Fig. 3 for a number of values of the parameter  $a_1$  equal to the ratio of the average distance  $\bar{r}$  between ions to the Debye radius  $d$ .

$\xi_1$  has a clear physical meaning. The NI cannot exist in the entire volume of the plasma. They are prevented from coming close to the positive ions, to a distance smaller than a certain critical value corresponding to the electric field  $\epsilon_{cr}$ , by the disintegrating action of this field. The presence of such a critical distance leads to the appearance of a correction to the statistical weight of the NI, equivalent in essence to the Van-der-Waals correction for the self-volume.

#### 4. DISCUSSION OF RESULTS

**Shift of photodetachment threshold.** In the experiment, the influence of the surrounding particles on the NI can be manifest in two ways. First, in the observed shift of the photodetachment threshold and, second, in the decrease of the magnitude of the photodetachment continuum, which is connected with the decrease of the effective statistical weight of the NI. Let us examine the first of these effects.

A certain decrease of the value of the photodetachment threshold of  $\Gamma$  in a plasma, compared with the value of the affinity energy determined by the method of crossed beams [16], was observed in [15] in a measurement of the spectra of the photodetachment of NI of atomic halogens. This decrease  $\Delta A$  amounted to  $0.01 \pm 0.003$  eV. The value of  $\Delta A$  was determined, generally speaking, by the difference between  $\Delta \bar{U}$  (34) and  $\Delta E$  (23) or (23a), but under the conditions of [15] they had  $\Delta E \ll \Delta \bar{U}$  and  $\Delta A$  was determined by the value of  $\Delta \bar{U}$ . An estimate of  $\Delta \bar{U}$  for firm NI of the  $\Gamma$  type can be obtained from formula (32), assuming the upper limit in the integrals to be infinite; this does not affect the result greatly, since  $\epsilon_{cr}$  for  $\Gamma$  is large. We obtain

$$\Delta \bar{U} \cong 2.88e^2 (2\alpha)^{1/2} \left( \frac{4\pi n_i}{3} \right)^{1/2} \quad (34a)$$

The shift of the threshold of  $\Gamma$  under the conditions of [15], calculated in accordance with (34a), is close to 0.01 eV, which agrees with [15]. The value of  $\alpha$  for  $\Gamma$  was taken from the data of [3].

In the case of weakly-bound NI, the Stark shift  $\Delta E$  and the effective lowering of the barrier  $\Delta \bar{U}$  can be appreciable. At the same time, however, the shift of the photodetachment threshold may turn out to be small, since  $\Delta E$  and  $\Delta \bar{U}$  for weakly-bound NI are close to each other. Experimental observation of the shift of the photodetachment threshold of weakly-bound NI is practically impossible, since this shift lies in the infrared region of the spectrum, where the threshold jump of the photodetachment cross section is smeared out by the contribution of other processes.

**Decrease of the photodetachment continuum.** In [17, 18] they measured the intensity of the emission of a plasma of nitrogen and air, and an appreciable fraction of the radiation was determined under the conditions of [17] by the photorecombination of the nitrogen atom with an

electron to form the negative ion  $N^-$ . The concentration of the charged particles in<sup>[17]</sup> was  $10^{16}$ – $10^{17}$   $cm^{-3}$ . In<sup>[18]</sup>, where the measurements were performed at pressures exceeding the pressure in<sup>[17]</sup> by 1.5–2 orders of magnitude, the concentration of the charged particles reached  $10^{18}$ – $10^{19}$   $cm^{-3}$ , and no radiation connected with photorecombination and formation of  $N^-$  was observed. This fact apparently indicates that under the conditions of<sup>[18]</sup> the concentration of the negative ion  $N^-$  becomes much lower than that calculated without allowance for the disintegration by the microfields. In view of the considerable uncertainty in the binding energy of  $N^-$  <sup>3</sup>P, the factor  $\xi_1$  for the conditions of<sup>[17,18]</sup> was estimated at three values of the binding energy A: 0.05, 0.1, and 0.15 eV. The results for the negative ion  $N^-$  are given in the table.

T, °K	A, eV	p = 100 atm <sup>[17]</sup>		p = 100 atm <sup>[18]</sup>	
		$n_e, 10^{17} cm^{-3}$	$\xi_1$	$n_e, 10^{17} cm^{-3}$	$\xi_1$
12000	0.05	0.7	1–0.9	16	0.4–0.2
	0.10		1–1		0.8–0.6
	0.15		1–1		0.9–0.8
16000	0.05	1.9	0.9–0.8	89	0.07–0.02
	0.10		1–0.9		0.3–0.1
	0.15		1–1		0.6–0.2

The table shows for each value of A, T, and p a pair of values of the factor  $\xi_1$ . The first corresponds to a = 1 and the second to a = 1/2. At a binding energy smaller than 0.1 eV we get under the conditions of<sup>[18]</sup>  $\xi_1 \ll 1$ , which explains qualitatively why no continuum connected with the photodecay of  $N^-$  was observed in<sup>[18]</sup>.

I am grateful to L. M. Biberman, G. É. Norman, A. N. Starostin, O. B. Firsov, and I. T. Yakubov for useful discussions.

<sup>1</sup>H. R. Griem, Phys. Rev., 128, 997 (1962).  
<sup>2</sup>G. Ecker and W. Kröll, Phys. Fluids 6, 62 (1963).  
<sup>3</sup>I. V. Avilova and G. É. Norman, Teplofizika Vysokikh Temperatur 2, 517 (1964).

<sup>4</sup>A. A. Likal'ter, Zh. Eksp. Teor. Fiz. 56, 240 (1969) [Sov. Phys.-JETP 29, 133 (1969)].  
<sup>5</sup>L. P. Kudrin and Yu. A. Tarasov, ibid. 43, 1504 (1962) [16, 1062 (1963)].  
<sup>6</sup>L. É. Pargamanik and G. M. Pyatigorskii, ibid. 44, 2029 (1963) [17, 1365 (1963)].  
<sup>7</sup>E. Salpeter, Phys. Rev., 87, 328 (1952).  
<sup>8</sup>B. L. Timan, Zh. Eksp. Teor. Fiz. 27, 740 (1954).  
<sup>9</sup>B. M. Smirnov, Atomnye stolkoveniya i élementarnye protsessy v plazmy (Atomic Collision and Elementary Processes in Plasma), Atomizdat, 1968.  
<sup>10</sup>C. Roothaan and P. Kelly, Phys. Rev., 131, 1177 (1963).  
<sup>11</sup>I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, 1963.  
<sup>12</sup>A. C. Riviere and D. R. Sweetman, Phys. Rev. Lett., 5, 560 (1960).  
<sup>13</sup>V. A. Oparin, R. N. Il'in, I. T. Serenkov, E. S. Solov'ev, and N. V. Fedorenko, ZhETF Pis. Red. 12, 237 (1970) [JETP Lett. 12, 162 (1970)].  
<sup>14</sup>C. F. Hooper, Jr., Phys. Rev., 149, 77 (1966); 165, 215 (1968).  
<sup>15</sup>R. S. Berry, et al., J. Chem. Phys., 35, 2237 (1961); 37, 2278 (1962); 38, 1540 (1963).  
<sup>16</sup>B. W. Steiner, M. L. Seman, and L. M. Branscomb, J. Chem. Phys., 37, 1200 (1962).  
<sup>17</sup>G. Boldt, Z. Physik, 154, 330 (1959). É. A. Asinovskii, A. V. Kirillin, and G. A. Kobzev, J. Quant. Spectr. Radiat. Transfer, 10, 143 (1970). J. C. Morris, et al., Phys. Rev. 180, 167 (1969). R. Allen, A. Textoris, J. Chem. Phys. 40, 3445 (1964). G. Thomas and W. Menard, AIAA J. 5, No. 12 (1967).  
<sup>18</sup>A. A. Kon'kov, A. P. Ryazin, and V. S. Rudnev, J. Quant. Spectr. Radiat. Transfer 7, 345 (1967). A. A. Kon'kov and A. P. Ryazin, 2-ï Vsesoyuznaya konferentsiya po fizike nizkotemperaturnoi plazmy (Second All-union Conference on Low Temperature-Plasma Physics), Minsk, 1968.