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ENERGY-LEVEL SHIFTS AND THE EQUATION OF STATE OF A PLASMA

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By means of the two-particle Green's function, a study is made of the level shifts of one-electron atoms in a plasma and of the equation of state of a Debye plasma. It is shown that low energy states experience a shift proportional to the root of the density and to the ratio kT/E_n for the case when this ratio is small. The shift of the ground state of particles of charge $z-1$ leads (in thermodynamic functions) to a correction that exceeds earlier obtained corrections to the Debye term if the densities of such particles are comparable with the electron density in the plasma.

THE level shift of single-electron atoms and ions in a plasma was investigated by Pargamanik[1] with the aid of a one-particle Green's function, with one ion separated and the plasma considered in the Coulomb field of this ion. The change in the energy of the one-electron excitations represented a shift in the energy levels of the atoms in the plasma. However, the value of the shift obtained thereby is incorrect. In the present paper the level shift of the bound states is determined with the aid of four-dimensional perturbation theory on the basis of the Bethe-Salpeter equation.

The diagram technique was successfully employed recently for an investigation of the equation of state of both classical[2,3] and quantum systems [4-6]. However, for a more correct investigation of the contribution of the bound states to the thermodynamic functions of the plasma, the latter are best calculated with the aid of the two-particle Green's function. We consider in this paper first a particle system with short-range forces, and then a particle system with Coulomb interaction.

1. LEVEL SHIFT

A. Perturbation theory. Let us consider a system of Coulomb particles in a volume V in the state of thermodynamic equilibrium at a temperature $T = 1/\beta$. The bound states of the particles are described by a two-particle Green's function whose poles determine the levels of the discrete spectrum. Let us consider also thermodynamic conditions by which the bound systems made up of an ion with charge z and an electron predominate in the plasma. If the energy of interaction of such a system with the plasma is sufficiently small, then the indicated poles can be determined by perturbation theory. In the zeroth approximation the potential is of the Coulomb type, and the equation for the Green's function has in momentum space the form

$$\begin{aligned} &G_2(p_1, p_2; p_3, p_4) \\ &\quad = (2\pi)^3 \beta G_0(p_1) G_0(p_2)\, \delta(p_1 - p_3)\, \delta(p_2 - p_4) \\ &\quad - (2\pi)^3 \beta G_0(p_3) G_0(p_4)\, \delta(p_1 - p_4)\, \delta(p_2 - p_3) \\ &\quad - \frac{G_0(p_1) G_0(p_2)}{(2\pi)^3 \beta} \sum_{q_4} \int d\mathbf{q}\, V(q)\, G_2(p_1 + q, p_2 - q; p_3, p_4). \end{aligned} \tag{1}$$

Changing over to the relative variables

$$p = \tfrac{1}{2}(p_1 - p_2),$$

$$p = \tfrac{1}{2}(p_3 - p_4), \qquad g = p_1 + p_2 = p_3 + p_4 \tag{1'}$$

and defining the function

$$\psi(p + g/2, g/2 - p, g/2 + p', g/2 - p') \equiv \psi(p, p', g$$

as

$$\psi(p, p', g) = G_2(p, p', g)\, G_0^{-1}(g/2 + p')\, G_0^{-1}(g/2 - p'),$$

we obtain an equation for $\psi(p, p', g)$:

$$\begin{aligned} &\psi(p, p', g) \\ &\quad = \frac{G_0(g/2 + p)\, G_0(g/2 - p)}{(2\pi)^3 \beta} \sum_{q_4} \int d\mathbf{q}\, U(q)\, \psi(p - q, p', g) \\ &\quad + (2\pi)^3 \beta \delta(p - p'). \end{aligned} \tag{2}$$

Let us introduce the three-dimensional function

$$\psi(\mathbf{p}, \mathbf{p}', g) = \sum_{p_4} \psi(p, p', g).$$

Summing both halves of (2) over p_4 ($p_4 = (2n+1)\pi/\beta$), we obtain an equation for $\psi(\mathbf{p}, \mathbf{p}', g)$:

$$\begin{aligned} &\psi(\mathbf{p}, \mathbf{p}', g) \\ &\quad = \frac{1}{(2\pi)^3} \frac{1}{i g_4 - g^2/4m - p^2/m + 2\mu} \int d\mathbf{q}\, U(\mathbf{q})\, \psi(\mathbf{p} - \mathbf{q}, \mathbf{p}', q) \\ &\quad + (2\pi)^3 \delta(\mathbf{p} - \mathbf{p}'). \end{aligned} \tag{3}$$

Summation over p_4 is carried out here and throughout by a procedure described in Fradkin's paper [4]. The function $G_0(p)$ has the form

$$G_0(p) = \frac{\delta\,[p_4 - (2n+1)\,\pi/\beta]}{-ip_4 - \mu + \varepsilon_p}$$

Putting $ig_4 - g^2/4m + 2\mu = E'$, we can see that Eq. (3) coincides with the Schrödinger inhomogeneous equation for the relative motion of two particles; the eigenvalues of this equation determine the unperturbed energy levels.

To analyze the interaction between an atom or an ion with a plasma, we add to the kernel of the integral equation (2) (U) a supplementary interaction ΔU, which depends generally speaking on q_4. To find the energy shift due to $\Delta U(\mathbf{q}, q_4)$ we can construct a perturbation theory analogous to the four-dimensional perturbation theory in quantum electrodynamics [7].

Let $\psi_n(\mathbf{p})$ be the wave function and E_n the eigenvalue of some stationary state, described by the Schrödinger equation

$$[F_n(\mathbf{p}) - L_0]\,\psi_n(\mathbf{p}) = 0, \tag{4}$$

$$L_0\psi_n = \frac{1}{(2\pi)^3}\int d\mathbf{q}\; U(\mathbf{q})\,\psi_n(\mathbf{p}-\mathbf{q}, \mathbf{p}', g),$$

$$F_n(\mathbf{p}) = E_n - \frac{p^2}{m} \tag{5}$$

Analogously, Eq. (2), for this state has the form

$$[F_n(p) - L]\,\psi_n(p) = 0, \tag{6}$$

$$L\psi_n(p) = \frac{1}{(2\pi)^3\beta}\sum_{q_4}\int d\mathbf{q}\; U(q)\,\psi_n(p-q, p', g). \tag{7}$$

Then the eigenfunction $\psi_n(p)$ corresponding to the state n can be written in the form

$$\psi_n(p) = \frac{E_n - \varepsilon_p}{{}_n(p)\,\beta}\,\psi_n(\mathbf{p}). \tag{8}$$

For a certain constant value E'_Δ, not coinciding with E_n we introduce two new functions

$$\psi_n^\Delta(p) = \frac{E'_\Delta - \varepsilon_p}{F_\Delta(p)\,\beta}\,\psi_n(\mathbf{p}), \qquad \widetilde{\psi}_n^\Delta(p) = \frac{E'_\Delta - \varepsilon_p}{F_\Delta(p)\,\beta}\,\psi_n^*(\mathbf{p}), \tag{9}$$

where F_Δ corresponds to the value of E_Δ.

Let

$$U(q) = U(\mathbf{q}) + \Delta U(\mathbf{q}, q_4). \tag{10}$$

and let the solution of the corresponding perturbed equation be the function $\psi_n(p)$ [which coincides with the function $\psi_n(p)$ when $\Delta U \to 0$]. Let further the eigenvalue of the energy corresponding to this solution be

$$E_\Delta = E_n + \Delta E_n. \tag{11}$$

Writing down the perturbed state in operator form, we have

$$[F_\Delta - L_0 - \Delta L]\,\Psi_n(p) = 0. \tag{12}$$

Acting on ψ_n^Δ by the operator $F_\Delta - L_0$ we obtain

$$(F_\Delta - L_0)\,\psi_n^\Delta = (E_\Delta - E_n)\,\psi_n/\beta, \tag{13}$$

$$\widetilde{\psi}_n^\Delta\,(F_\Delta - L_0) = (E_\Delta - E_n)\,\psi_n^*/\beta. \tag{14}$$

We introduce a new function

$$\psi_\Delta = \Psi_n - \psi_n^\Delta. \tag{15}$$

Then (12) assumes the form

$$(F_\Delta - L_0)\,\psi_n^\Delta + (F_\Delta - L_0)\,\psi_\Delta = \Delta L\psi_n^\Delta + \Delta L\psi_\Delta. \tag{16}$$

Inasmuch as $\Delta L\psi \ll L_0\psi$ and $\Delta E_n \ll E_n$, we get $\psi_\Delta \ll \psi_n^\Delta$ and $\psi_n^\Delta \approx \psi_n$. Multiplying (16) from the left by ψ_n^Δ we obtain with account of (11), (12), and (14),

$$\Delta E_n\beta^{-1}\psi_n^*\,(\psi_n^\Delta + \psi_\Delta) = \widetilde{\psi}_n^\Delta\,\Delta L\,(\psi_n^\Delta + \psi_\Delta). \tag{17}$$

Neglecting in (17) terms of second order of smallness, we obtain after summation over p_4

$$\frac{\Delta E_n}{\beta}\,\psi_n^*(\mathbf{p})\,\psi_n(\mathbf{p}) = \sum_{p_4}\widetilde{\psi}_n(p)\,\Delta L\psi_n(p). \tag{18}$$

Integration of (18) with respect to **p** leads to the following expression for the shift:

$$\Delta E_n = \frac{1}{(2\pi)^3}\sum_{p_4, q_4}\int d\mathbf{p}\,d\mathbf{q}\;\widetilde{\psi}_n(p)\,\Delta U(\mathbf{q}, q_4)\,\psi_n(p-q). \tag{19}$$

It is easy to see that in the case when ΔU is independent of q_4, formula (19) gives the usual correction to the energy in first order of perturbation theory for the Schrödinger equation.

We can show analogously that in the presence of degenerate unperturbed states the shift ΔE must be found from the secular equation

$$\sum_{n'}(V_{nn'} - \Delta E\,\delta_{nn'})\,c_{n'} = 0, \tag{20}$$

where n and n′ run through all the values pertaining to the unperturbed level E_n, and

$$V_{nn'} = \frac{1}{(2\pi)^3\beta^2}\sum_{p_4, p'_4}\int d\mathbf{p}\,d\mathbf{p}'\,\frac{(E_n - \varepsilon_p)(E_n - \varepsilon_{p'})}{F_n(p)\,F_n(p')}$$

$$\times\,\psi_n^*(\mathbf{p})\,\Delta U(p, p')\,\psi_{n'}(\mathbf{p}'). \tag{21}$$

Subsequently, the nondiagonal matrix elements drop out, since ΔU is independent of the angles for small values of **q**.

B. Calculation of the level shift. In the case of two different bound particles (ion with charge z and electron) we must write

$$\sum_{p_4}\frac{1}{F(p)} = \sum_{p_4} G_0^i\left(\frac{m_0}{m}g + p\right) G_0^e\left(\frac{m_0}{m}g - p\right)$$

$$\approx \beta\left(ig_4 - \frac{p^2}{2M} - \frac{p^2}{2m} - \frac{g^2 m_0}{2mM} + \mu_e + \mu_i\right)^{-1},$$

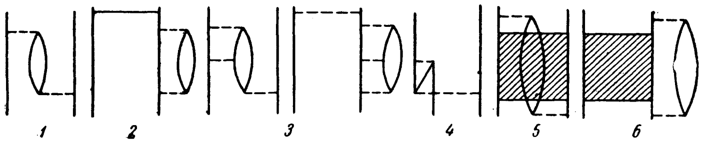

FIG. 1

where $m_0 = mM/(m+M)$, and μ_e and μ_i are the chemical potentials of the electrons and ions.

The largest terms which contribute to ΔU, i.e., the terms proportional to the first power in the density, are represented by the diagrams shown in Fig. 1. The loops in these diagrams can be electronic (e), ionic (i), or "atomic" (a) and can be inserted in both lines. For example, for a diagram of type 1 with ionic loop, ΔU has the form

$$\Delta U(\mathbf{q}, q_4) = \frac{1}{(2\pi)^3\beta}\sum_{p_4}\int G_0^i(p)\, G_0^i(p+q)\, V_{ii}(q)\, V_{ie}(q)\, d\mathbf{p}\,.$$

The expression for $\Sigma(g/2+p)$, corresponding to diagram 2, is written as

$$\Sigma^i\left(\frac{g}{2}+p\right) = \frac{1}{(2\pi)^6\beta^2}\sum_{(p_1)_4 q_4}\int G_0^i(p_1)\, G_0^i(p_1+q)$$

$$\times G_0^i\left(p-q+\frac{g}{2}\right)V_{ii}(q)\, d\mathbf{p}_1 d\mathbf{q}.$$

It is easy to see that diagrams of type 1—3, 5, and 6 give expressions that diverge at small momenta $\mathbf{q}$, and to eliminate this divergence it is necessary to sum chains of loops of type e, i, and a. As a result we obtain effective interaction "potentials" $V^*(\mathbf{q}, q_4)$. For example, the potential for the ee interaction has the form

$$V^*_{ee}(\mathbf{q}, q_4) = \frac{V_{ee}(\mathbf{q})}{1 - V_{ee}[\Pi_e + z^2\Pi_i + (z-1)^2\Pi_a]}, \tag{22}$$

where the electronic loop is

$$\Pi_e(\mathbf{q}, q_4) = \frac{1}{(2\pi)^3}\int d\mathbf{p}\,\frac{n^e_{\mathbf{p}+\mathbf{q}} - n^e_{\mathbf{p}}}{iq_4 + \varepsilon^e_{\mathbf{p}} - \varepsilon^e_{\mathbf{p}+\mathbf{q}}}. \tag{23}$$

and $n_p = \exp[-\beta\epsilon_p]$ for Boltzmann statistics.

It is essential that when $\mathbf{q} \to 0$ the quantity $\Pi(\mathbf{q}, q_4)$ differs from zero for $q_4 = 0$. Therefore in summing over q_4 the terms with $q_4 = 0$ make the largest contribution. Terms of this type give a contribution proportional to the lowest power of the density.

The calculation of the shift using diagrams 1 with a chain instead of a loop, i.e., when ΔU has the form $\Delta U(\mathbf{q}, q_4) = V^*(\mathbf{q}, q_4) - V(\mathbf{q})$, where $V(\mathbf{q}) = 4\pi e^2/q^2$ is the Coulomb potential, leads to the result (in the c.m.s.)

$$\Delta E_n = -\frac{2}{(2\pi)^3\beta}ze^2\varkappa\int\frac{d\mathbf{p}\,\psi_n(\mathbf{p})\,\psi_n^*(\mathbf{p})}{E_n - \varepsilon_p},$$

$$\varkappa^2 = 4\pi e^2\beta\,[n_e + z^2 n_i + (z-1)^2 n_a]. \tag{24}$$

Diagrams of type 2 yield the same expression with z replaced by z^2+1.

Substituting the wave functions in the form

$$\psi_{n,l,m}(\mathbf{p}) = F_{nl}(\mathbf{p})\, V_{l,m}(\theta, \varphi),$$

$$F_{nl}(\mathbf{p}) = \left[\frac{2}{n}\frac{(n-l-1)!}{(n+l)!}\right]^{1/2}$$

$$\times\, n^2 2^{2(l+1)}\, l!\,\frac{n^l p^l}{(n^2p^2+1)^{l+2}}\, C^{l+1}_{n-l-1}\left(\frac{n^2p^2-1}{n^2p^2+1}\right),$$

where $C^\nu_N(x)$ is the Gegenbauer function[8], we obtain the expressions for the level shift.

For the S-states we have

$$\Delta E_{n0} = \begin{cases} -\dfrac{5}{4}\left(\dfrac{z-1}{z}\right)^2\dfrac{a_0\varkappa}{\beta} & \text{for } n=1 \\ -\dfrac{3}{2}\left(\dfrac{z-1}{z}\right)^2\dfrac{a_0\varkappa}{\beta}n^2 & \text{for } n=2,3,4\ldots \end{cases} \tag{25}$$

where a_0 is the Bohr radius of the hydrogen atom. For $n = 2$ and $l \neq 0$ we get

$$\Delta E_{20} = -6\left(\frac{z-1}{z}\right)^2\frac{a_0\varkappa}{\beta}, \quad \Delta E_{21} = -\frac{14}{3}\left(\frac{z-1}{z}\right)^2\frac{a_0\varkappa}{\beta}. \tag{25'}$$

Diagrams of type 3 give the following shift for the S-states

$$\Delta E_{n0} = \begin{cases} \dfrac{7\pi}{2}e^2a_0^2\dfrac{(z-1)^3}{z^4}[z^3n_i + (z-1)^3n_a - n_e]\ln\dfrac{1}{e^2\varkappa\beta} \\ \dfrac{5\pi}{z^4}e^2a_0^2(z-1)^3[z^3n_i + (z-1)^3n_a - n_e]\ln\dfrac{1}{e^2\varkappa\beta} \end{cases}$$

for $n = 1$

for $n = 2, 3\ldots$ (26)

Likewise diverging at small $\mathbf{q}$ are diagrams of the type 5 and 6, where the shaded square denotes the effective potential[9]:

$$\Gamma(\mathbf{p}, \mathbf{p}', g) = 2(2\pi)^3\beta(E' - \varepsilon_{\mathbf{p}'})\sum_k\frac{(E_k - \varepsilon_{\mathbf{p}})\,\psi_k(\mathbf{p})\,\psi_k^*(\mathbf{p}')}{E' - E_k} \tag{27}$$

The calculation of the contribution of these diagrams leads to the result

$$\Delta E_n = \frac{4\pi e^2(z-1)^2\varkappa^2}{(2\pi)^3\beta}\int\frac{dq}{\mathbf{q}^2(\mathbf{q}^2+\varkappa^2)}$$

$$\times\sum_k\int\frac{d\mathbf{p}\,d\mathbf{p}'\,\psi_n(\mathbf{p})\,\psi_n^*(\mathbf{p}')\,(E_k - \varepsilon^e_{\mathbf{p}})\,\psi_k^*(\mathbf{p})\,\psi_k(\mathbf{p}')}{(E_n - \varepsilon^e_{\mathbf{g}})(ig_4 - \varepsilon^i_{\mathbf{q}} - E_k + \mu_e + \mu_i)}. \tag{28}$$

When $n \neq k$ we get $\Delta E_n = 0$, and when $n = k$ we get

$$\Delta E_n = -\tfrac{1}{4}(z-1)^2 e^2\varkappa/\varepsilon_g\beta\,. \tag{29}$$

To explain the meaning of expression (29), let us calculate the proper energy of the free electron

$$\Sigma^e(p) = \frac{1}{(2\pi)^3\beta}\sum_{q_4}\int d\mathbf{q}G_0^e(p-q)\,[V^*(\mathbf{q}, q_4) - V(\mathbf{q})]\,.$$

Calculation at small values of q yields

$$\Sigma^e(p) \doteq -e^2\varkappa/4\varepsilon_{\mathrm{p}}\beta.$$

Consequently, ΔE_n in (29) is a correction to the proper energy of the "atom," i.e., an ion with charge $z-1$ moving freely. Indeed, averaging (29) over the Maxwellian distribution yields the Debye energy of an ion with charge $z-1$:

$$\Delta E = -\tfrac{1}{2}(z-1)^2 e^2\varkappa\,. \tag{30}$$

This shift is independent of the state of the "atom." The exchange diagrams, for example of type 4, give expressions that converge for all values of **q**, and the shift is of order $(a_0\kappa)^2/\beta$, which agrees with the usual calculation of the exchange integral for helium, as carried out by the authors.

It follows from (25) and (25′) that the level shift is proportional to the square root of the density and increases with temperature like $\sqrt{T}$. The shift also increases with increasing principal quantum number. There is no such effect for hydrogen $(z = 1)$, something physically obvious in view of the short-range interaction of the neutral hydrogen atom with the plasma.

The magnitude of the effect can be judged from a comparison of the shift with the linear Stark splitting

$$\Delta_S \sim ne^2a_0r_0k^2, \tag{31}$$

where k is the principal quantum number and r_0 the mean distance between particles. It is easy to see that

$$\Delta_S/\Delta E_n \sim \varkappa r_0 \ll 1.$$

The condition for the applicability of perturbation theory has the form

$$\Delta E_n/E_n \ll 1.$$

It must be noted that in the derivation of the expression for the shift we have neglected $\epsilon_g \sim kT$ compared with E_n. The formulas obtained are therefore valid at sufficiently low temperatures, $kT/E_n \ll 1$.

2. EQUATION OF STATE

A. System of particles with short-range forces. Let us consider a system of interacting particles in a volume V in a state of thermodynamic equilibrium at a temperature T. The Hamiltonian of the system is $H = H_0 + H_1$, where H_0 is the Hamiltonian of the noninteracting particles and H_1 is the interaction Hamiltonian:

$$H_1 = \frac{g'}{2}\int\bar{\psi}(x_1)\,\bar{\psi}(x_2)\,U(x_1 - x_2)\,\psi(x_1)\,\psi(x_2)\,. \tag{32}$$

Here $U(x_1 - x_2) = U(\mathbf{x}_1 - \mathbf{x}_2)\,\delta(t_1 - t_2)$ is the pair interaction potential and g' is the interaction constant.

The partition function of the system has the form

$$Z = \mathrm{Sp}\, e^{-\beta(H-\mu N)} = e^{-\beta\Omega}, \tag{33}$$

where μ is the chemical potential, Ω is the thermodynamic potential, and N is the total number of particles in the system.

It is easy to see that Ω can be expressed in terms of the two-particle Green's function in the form

$$\Omega = \Omega_0 - \frac{1}{2(2\pi)^9\beta^3}\int_0^{g'}\frac{dg'}{g'}\int G_2(p_1p_2;\, p_3p_4)$$

$$\times\, U(p_1 - p_3)\, dp_1dp_2dp_3\,, \tag{34}$$

where $p_4 = p_1 + p_2 - p_3$ and Ω_0 is the thermodynamic potential of the ideal system.

The equation for G_2 is given in the "ladder" approximation by formula (1). Introducing the function

$$Q(p_1p_2;\, p_3p_4) = G_2(p_1p_2;\, p_3p_4)\, G_0^{-1}(p_3)\, G_0^{-1}(p_4)$$

and going over to the "center of mass" system (1′), we obtain

$$\Delta\Omega = \frac{1}{2(2\pi)^9\beta^3}\int_0^{g'}\frac{dg'}{g'}\int\varphi(p', g)\, U(p' - p)$$

$$\times\, Q(p, p', g)\, dp\, dp'\, dg\,,$$

$$\varphi(p, g) \equiv G_0(g/2 + p)\, G_0(g/2 - p)\,. \tag{35}$$

The equation for

$$Q(g/2 + p, g/2 - p, g/2 + p', g/2 - p') \equiv Q(p, p', g)$$

has the form

$$Q(p, p', g) = (2\pi)^3\,[\delta(p - p') + \delta(p + p')]$$

$$+ \frac{\varphi(p, g)}{(2\pi)^3\beta}\sum_{q_4}\int dq\, U(\mathbf{q})\, Q(p - q, p', g)\,. \tag{36}$$

Let us sum over p_4 in (36), recognizing that $U(p)$ is independent of the fourth momentum component. Putting

$$Q(\mathbf{p}, \mathbf{p}', g) = \Sigma_{p_4} Q(p, p', g),$$

we obtain

$$\Delta\Omega = \frac{1}{2(2\pi)^9\beta^2}\int_0^{g'}\frac{dg'}{g'}\int\varphi(p', g)$$

$$\times\, U(\mathbf{p}' - \mathbf{p})\, Q(\mathbf{p}, \mathbf{p}', g)\, d\mathbf{p}d\mathbf{p}'dg\,. \tag{37}$$

We introduce the function

$$\chi(\mathbf{p}) = \Gamma(\mathbf{p}) / (E' - p^2/m),$$

where

$$\Gamma(\mathbf{p}) = \int U(\mathbf{p}' - \mathbf{p})\, Q(\mathbf{p}')\, d\mathbf{p}',$$

$$E' = ig_4 - \frac{g^2}{4m} + 2\mu. \tag{38}$$

The equation for χ has the form of an inhomogeneous Schrödinger equation

$$\left(E' - \frac{p^2}{m}\right)\chi(\mathbf{p}_2) - \frac{1}{(2\pi)^3}\int U(\mathbf{p}_1 - \mathbf{p}_2)\,\chi(\mathbf{p}_1)\,d\mathbf{p}_1$$
$$= (2\pi)^3 \beta\,[U(\mathbf{p}' - \mathbf{p}_2)' + U(\mathbf{p}' + \mathbf{p}_2)]. \tag{39}$$

Expressing the solution of (39) in terms of the wave functions of the relative motions of the particles, substituting it in (35), summing over p_4 and g_4, and integrating with respect to $\mathbf{g}$, we obtain in the case of Boltzmann's statistics

$$\Delta\Omega = \frac{e^{2\mu\beta}}{(2\pi)^3}\left(\frac{m}{\pi\beta}\right)^{3/2}\int_0^{g'}\frac{dg'}{g'}\int d\mathbf{p}\sum_k e^{-\beta E_k}$$
$$\times\left(E_k - \frac{p^2}{m}\right)\psi_k(\mathbf{p})\psi_k^*(\mathbf{p}). \tag{40}$$

This is an analogue of the well known formula of Bethe and Uhlenbeck for the second virial coefficient in the quantum case.

In the quasi-classical limit we obtain as a result of simple calculation

$$\Delta\Omega = \frac{e^{2\mu\beta}}{16}\left(\frac{m}{\pi\beta}\right)^3\int_0^1\frac{d\lambda}{\lambda}\int_0^\infty 4\pi r^2\lambda U(r)e^{-\beta\lambda U(r)}dr$$
$$= -\frac{n^2}{2\beta}\int_0^\infty (e^{-\beta U} - 1)\,4\pi r^2 dr, \quad n = e^{\beta\mu}(m/2\pi\beta)^{3/2}. \tag{41}$$

Formula (41) coincides with the expression for $\Delta\Omega$, due to the second virial coefficient, in the classical case.

B. System of particles with Coulomb interaction. Inasmuch as the Coulomb forces are long-range, we cannot confine ourselves to pair interactions even in the first term of the expansion of the thermodynamic quantities in powers of the gas density. It is necessary to take into account the influence of many Coulomb particles.

Let us consider a system of electrons against the background of a uniformly distributed positive charge. For correct account of the interaction it is necessary to introduce an effective potential of the form (22), which represents a "chain" of electronic loops (23).

Inasmuch as in the present problem the significant distances are $e^2\beta \gg a_0$ (where a_0 is the Bohr radius), we can consider the adiabatic approximation. We assume that $U^*(\mathbf{q}, q_4)$ does not depend on q_4. We then have in the Debye limit $\Pi(\mathbf{q}, q_4) \to -\beta n$, where n is the electron density. After calculations analogous to those made in Sec. 1, we obtain for $\Delta\Omega$

$$\Delta\Omega = \frac{e^{2\mu\beta}}{(2\pi)^3}\left(\frac{m}{\pi\beta}\right)^{3/2}\int_0^{e^2}\frac{de^2}{e^2}\int d\mathbf{p}\,d\mathbf{p}'U(\mathbf{p} - \mathbf{p}')$$
$$\times\sum_k e^{-\beta E_k}\psi_k(\mathbf{p}')\,\psi_k(\mathbf{p}), \tag{42}$$

where $\psi_k(\mathbf{p})$ are the wave functions for a Debye potential with charge $e\sqrt{\lambda}$, where $0 \leq \lambda \leq 1$.

Expression (42) converges if we subtract from it the first perturbation-theory term $\Delta\Omega_0 = n^2U(0)/2$, which drops out in a real plasma because it is specified to be quasi-neutral. In the quasi-classical case $e^2/\hbar v \gg 1$ we obtain in analogy with Section 1 the following expression for $\Delta\Omega$:

$$\beta\Delta\Omega = 2\pi n^2(e^2\beta)^3\int_0^1\lambda^2 d\lambda\int_0^\infty t\,dt\,\{\exp(t^{-1}e^{-\alpha t}) - 1\}, \tag{43}$$

where $\alpha = \beta e^2\kappa\lambda^{3/2} \ll 1$.

In the expansion of (43) in α we retain the terms with negative powers of α and the terms proportional to $\ln\alpha$. As a result we obtain after integration with respect to λ

$$-\beta\Delta\Omega = \frac{2}{3}\sqrt{\pi\beta^3}e^3n^{3/2} - \frac{1}{3}\pi(e^2\beta)^3 n^2\ln(\beta e^2\varkappa), \tag{44}$$

which coincides with formula (12) of the paper by Vedenov and Larkin[5].

Let us consider a multi-component system made up of atoms, electrons, and ions. In this case we have for $\Delta\Omega$ an expression of the form

$$-\Delta\Omega = \frac{1}{2}\int_0^{e^2}\frac{de^2}{e^2}\int dp_1\,dp_2\,dp_3\,U(p_3 - p_1)$$
$$\times\sum_{ij} g_{ij}G_2^{ij}(p_1, p_2; p_3, p_4), \tag{45}$$

where $p_4 = p_1 + p_2 - p_3$, g_{ij} is the constant of the interaction between the i-th and j-th components, while the functions G_2^{ij} are determined from equations such as (1). Formula (45) is supplemented by the conditions of equilibrium and quasi-neutrality of the plasma:

$$\mu_z + \mu_e = \mu_{z-1}, \qquad \sum_i q_i\frac{\partial\Omega_i}{\partial\mu_i} = 0,$$

where q_i is a charge of the particles of the i-th component.

Let us consider a case when the plasma contains electrons (e), ions with charge z (i), and (z − 1)-fold ionized atoms. The latter constitute a one-electron bound system and we shall henceforth merely call them "atoms" a. In this case the following interactions are present in the plasma: ee, ii, ie, aa, ea, and ia. The interaction with the repulsion potential is taken into account quasi-classically, in exactly the same manner as in the derivation of (44). As a result we obtain, for example for $\Delta\Omega_{ii}$:

$$-\beta\Delta\Omega_{ii}=\frac{2}{3}\sqrt{\pi\beta^3}\,e^3\frac{n_i^2z^2}{[n_e+z^2n_i+(z-1)^2n_a]^{1/2}}$$

$$+\frac{\pi}{3z^2}(\beta e^2z^2)^3\ln\frac{1}{\beta e^2z^2\varkappa},$$

$$\varkappa^2=4\pi e^2\beta\,[n_e+z^2n_i+(z-1)^2n_a]^{1/2}. \tag{46}$$

In the case of an attractive potential it is necessary to separate the contribution from the first discrete levels, and treat the remaining part quasi-classically. Changing over in the formula

$$\Delta\Omega_{ie}=-(2\pi)^{-3}ze^{\beta(\mu_e+\mu_i)}(m_i/2\pi\beta)^{3/2}$$

$$\times\int_0^1\frac{d\lambda}{\lambda}\int dp\,dp'\,U(p-p')\sum_k\exp(-\beta E_k^{ie})\psi_k^{ie}(p')\psi_k^{ie}(p) \tag{47}$$

to the quasi-classical treatment, starting with the level $E_{n_0}\gg 1$, we readily obtain the converging expression

$$-\beta(\Delta\Omega_{ie})_{\mathrm{qu}}=4\pi n_en_i(e^2\beta z)^3\int_0^1\lambda^2d\lambda\left\{\int_0^{t_{n_0}}\left[\exp\left(\frac{e^{-\alpha t}}{t}\right)\right.\right.$$

$$\times\left(1-\operatorname{erf}\sqrt{\frac{e^{-\alpha t}}{t}-\frac{1}{t_{n_0}}}\right)$$

$$\left.\left.+\frac{2}{\sqrt{\pi}}e^{-t_{n_0}}\sqrt{\frac{e^{-\alpha t}}{t}-\frac{1}{t_{n_0}}}-1\right]\right\}tdt$$

$$+\int_{t_{n_0}}^{\infty}\left[\exp\left(\frac{e^{-\alpha t}}{t}\right)-1\right]tdt;$$

$$t_{n_0}=2\delta n_0^2/\lambda^2,\qquad \delta=\hbar^2/\beta me^4z^2\ll 1,\qquad \alpha=\beta e^2z\varkappa\lambda^{3/2}\ll 1. \tag{48}$$

The expansion of (48) in α leads with the accuracy indicated above to the following expression for $\Delta\Omega_{ie}$, which does not depend on n_0:

$$-\beta(\Delta\Omega_{ie})_{\mathrm{qu}}=-\frac{4}{3}\sqrt{\pi\beta^3}\,e^3\frac{n_in_ez^2}{[n_e+z^2n_i+(z-1)^2n_a]^{1/2}}$$

$$-\frac{2\pi}{3z}(\beta e^2z)^3n_in_e\ln\frac{1}{\beta e^2z\varkappa}. \tag{49}$$

We calculate analogously the contribution from the quasi-classical part of the ea interaction.

The contribution from the ground state of the atom E_0, which in first approximation can be regarded as a Coulomb contribution, is already taken into account in Ω_0. The contribution to the equation of state from the shift of the ground level can be obtained by using four-dimensional perturbation theory. In this case the adiabatic approximation is no longer valid in view of the large velocity of orbital motion compared with thermal velocity.

C. Construction of thermodynamic perturbation theory. The expression for $\Delta\Omega$ can be written in the form

$$\Delta\Omega=\frac{1}{(2\pi)^6\beta}\int_0^{e^2}\frac{de^2}{e^2}\int\varphi(p_1,g)\,\Gamma(p_1,p_1,g)\,dp_1dg, \tag{50}$$

where Γ is defined by (38) and satisfies the equation

$$\Gamma(p,p',g)=(2\pi)^3\beta U(\mathbf{p}-\mathbf{p}')$$

$$+\frac{1}{(2\pi)^3\beta}\int V(p-p_1)\varphi(p_1,g)\Gamma(p_1,p',g)dp_1. \tag{51}$$

Let

$$\Gamma(p,p',g)=\Gamma_0(\mathbf{p},\mathbf{p}',g)+\Gamma_1(p,p',g),$$

with Γ_0 represented by a ladder with Coulomb potential U. Let further $V = U-\Delta U$, where ΔU is a small perturbation which depends generally speaking on the four momentum components.

Neglecting in (51) terms of second order of smallness, we obtain an equation for Γ_1:

$$\Gamma_1(p,p',g)=\frac{1}{(2\pi)^3\beta}\int U(p-p_1)\,\varphi(p_1,g)\,\Gamma_1(p_1,p',g)\,dp_1$$

$$+\frac{1}{(2\pi)^3\beta}\int\Delta U(p-p_1)\,\varphi(p_1,g)\,\Gamma_0(\mathbf{p}_1,\mathbf{p}',g)\,dp_1. \tag{52}$$

In first approximation we take into account the second term in the right half of (52), i.e.,

$$\Gamma_1^{(0)}=\frac{1}{(2\pi)^3\beta}\sum_{q_4}\int d\mathbf{q}\,\Delta U(\mathbf{q},q_4)\,\varphi(p-q,g)\,\Gamma_0(p-q,p',g). \tag{53}$$

It is easy to see that $\Gamma_1^{(0)}$ does not depend on p_4'. Solving (52) by the iteration method, we verify that Γ_1 is likewise independent of p_4'. For ΔU in the form of a loop $\Gamma_1^{(0)}$ has the form represented in Fig. 2 by diagram 1, where the shaded square corresponds to Γ_0.

In the second approximation Γ_1 is represented by diagram 3, etc., so that diagram 5 of Fig. 2 corresponds to a solution of Eq. (52) for Γ_1. Considering a solution of (52) for ΔU in the form 4, 5, etc., we obtain for Γ_1 a diagram of the form 6.

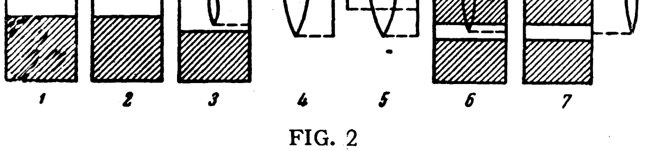

FIG. 2

Let

$$\chi(\mathbf{p}, \mathbf{p}', g) = \Gamma_1(\mathbf{p}, \mathbf{p}', g)\,\varphi(p, g). \tag{54}$$

The equation for χ has the form of a Schrödinger equation with right half

$$\Theta(\mathbf{p}, \mathbf{p}', g) = \frac{E' - \varepsilon_p}{(2\pi)^3\beta} \sum_{q_4, p_4} \varphi(p, g)$$
$$\times \int d\mathbf{q}\,\Delta U(\mathbf{q}, q_4)\,\varphi(p - q, g)\,\Gamma_0(\mathbf{p} - \mathbf{q}, \mathbf{p}', g), \tag{55}$$

so that the solution for χ is expressed in terms of the ψ-functions of relative motion of the particles.

Writing down for ΔU a chain in place of a loop, summing over the fourth momentum component, we obtain for $\mathbf{q} \to 0$ from (50), (54), and (55):

$$\Delta\Omega = \frac{1}{(2\pi)^6\beta}\int_0^{e^2}\frac{de^2}{e^2}\int d\mathbf{p}\,d\mathbf{p}_1\,dg\exp\{\beta(\mu_e + \mu_i - \varepsilon_g)\}$$
$$\times \sum_{n,k}\psi_n(\mathbf{p})\,\psi_k(\mathbf{p})\,(E_k' - \varepsilon_{\mathbf{p}_1})\,\psi_n^*(\mathbf{p}_1)\,\psi_k(\mathbf{p}_1)$$
$$\times\left\{\frac{(E_k' - \varepsilon_{\mathbf{p}})\exp(-\beta E_k)}{(E_k' - \varepsilon_{\mathbf{p}_1})^2} - \frac{(E_n' - \varepsilon_{\mathbf{p}})\exp(-\beta E_n)}{(E_n' - \varepsilon_{\mathbf{p}_1})^2}\right\}. \tag{56}$$

Accurate to the higher powers of the ratio $kT/E_n \ll 1$, the greatest contribution to ΔΩ is made by the term with $n = k$.

Separating in (56) the contribution of the ground state, we have

$$\Delta\tilde{\Omega} = \frac{\exp[\beta(\mu_e + \mu_i)]}{(2\pi)^3\beta}\,n_i n_e\left(\frac{m}{\pi\beta}\right)^{3/2} z\int_0^{e^2}\frac{de^2}{e^2}\,e^2\varkappa$$
$$\times \int (E_0 - \varepsilon_{\mathbf{p}})\,|\psi_0|^2 e^{-\beta E_0}\,d\mathbf{p}\int\frac{d\mathbf{p}_1\,|\psi_0(\mathbf{p}_1)|^2}{E_0 - \varepsilon_{\mathbf{p}_1}}. \tag{57}$$

Simple calculation yields

$$\Delta\tilde{\Omega} \approx 5a_0\varkappa n_a/2z\beta, \tag{58}$$

where n_a is the density of the "atoms."

We calculate analogously the correction to ΔΩ due to the self-energy part inserted in G_0^e and G_0^i, where in place of a loop we write a chain as before. As a result of such a calculation we obtain an expression of the type (57), where the coefficient $5/2z$ is replaced by $-5(z^2 + 1)/4z^2$. Calculation of diagram of the type 6 and 7 (Fig. 2) leads to the Debye term, due to the change in the energy of the ion with charge $z - 1$ as it moves as a unit. This term has already been taken into account before.

With account of (58), the expression for the thermodynamic potential of the system under consideration has the form

$$\beta\Omega = -\sum n_j - \frac{\varkappa^3}{12\pi} + \frac{\pi}{3}\beta^3\sum_{ij} n_i n_j (q_i q_j)^3 \ln\frac{1}{\beta q_i q_j \varkappa}$$
$$- \frac{5}{4}\left(\frac{z-1}{z}\right)^2 a_0\varkappa n_a. \tag{59}$$

Terms that are quadratic in the density $L \sim (e^2\beta)^3 n^2$ have been omitted. The ratio of L to the term due to the shift is proportional to $\alpha\gamma$, where $\alpha = e^2\kappa\beta \ll 1$ and $\gamma = \beta E_0 \gg 1$. The first condition is the stronger one, so that conditions exist when this ratio is small. For example, for He II at $T \approx 3$ eV and $P = 0.06$ atm we have $n_a \sim n_e/2 \approx 9 \times 10^{14}\ \text{cm}^{-3}$. In this case the ratio of L to the last term in (59) (L_1) is of order 10^{-2}, and the ratio of the logarithmic term to L_1 is about 10^{-1}. Thus, in the case when the number of "atoms" is comparable with the number of electrons, the term in ΔΩ due to the level shift is more appreciable than the remaining corrections to the Debye term.

We consider the following qualitative explanation of the studied effect to be possible. In the paper of Bohm and Pines[10] it is shown that an electron gas can be described in terms of the Fourier components of the electron density at each point of space, ρ_k, with ρ_k proportional to the fluctuations of the electron gas density ρ. In the general case $\rho_k = a_k q_k + \eta_k$, where the q_k are the collective coordinates and the η_k are the density fluctuations connected with the motion of the individual particles:

$$\eta_k = \sum\frac{\omega^2 - \omega_p^2 - (\mathbf{k}\mathbf{v}_i)^2}{\omega^2 - (\mathbf{k}\mathbf{v}_i)^2}\,e^{i\mathbf{k}\mathbf{x}_i}. \tag{60}$$

If we consider the contribution made to the density distribution by the s-th particle, then taking account of the well known dispersion formula $\omega^2 = \omega p^2 + k^2\langle v^2\rangle$, where ω_p is the Langmuir frequency and $\langle v^2\rangle$ is the square of the velocity averaged after Maxwell, we have

$$\eta_s(\mathbf{r}) \approx \sum_k\left\{\frac{k^2\langle v^2\rangle - (\mathbf{k}\mathbf{v}_s)^2}{\omega_p^2 + k^2\langle v^2\rangle - (\mathbf{k}\mathbf{v}_s)^2}\right\}e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}_s)}. \tag{61}$$

The calculation of η_s by means of formula (39) for the case of a slow particle leads, as is well known, to the ordinary Debye screening of its charge.

Let us consider as the s-th particle an electron moving on a circle of radius a with constant velocity $v_0 \gg \sqrt{\langle v^2\rangle} \equiv v_T$. Then, separating the δ-function in (61), we obtain

$$\eta_s(\mathbf{r}) = -\frac{\omega_p^2}{4\pi}e$$
$$\times\int\frac{\exp\{(x - a\cos\omega t)\,ik_x + (y - a\sin\omega t)\,ik_y + ik_z z\}}{\omega_p^2 + k^2\langle v^2\rangle - v_0^2(k_y\cos\omega t - k_x\sin\omega t)^2}\,d\mathbf{k}. \tag{62}$$

Solving the Poisson equation with charge density (62), we obtain the potential at the point of the electron. It turns out that the main term in the expansion of the resultant expression in powers of v_T/v_0 has for any fixed t the form

$$\varphi\,(a\cos\omega t,\ \ a\sin\omega t,\ 0,\ t) = -\mathrm{const}\cdot e\varkappa\, v_T/v_0 .$$

This indicates a weaker screening of a rapidly moving electron compared with Debye screening. Indeed, the same value of the potential at small distances would be obtained by expanding a potential of the form $\mathrm{const}\cdot\exp[-\kappa_1 r]/r$, where $\kappa_1 = \kappa v_T/v_0$.

Bearing in mind that to calculate the corrections to the energy it is necessary to know the potential at small distances, we write approximately

$$\tilde{\eta}_s\,(\mathbf{r}) = e\varkappa_1^2 e^{-\varkappa_1 r}/r. \qquad (63)$$

In our "atom" the electron revolves about a nucleus with charge z. This charge also polarizes the plasma. To find this effect we have the following equation[11]

$$\Delta\varphi - \varkappa^2\varphi = ez\delta\,(\mathbf{r}), \qquad (64)$$

solution of which yields the screening of the charge. Both effects from the electron and from the nucleus must be regarded simultaneously. Adding to the right half of (64) the charge density due to the polarization of the plasma by the electron, and the density of the electron itself, we get

$$\Delta\varphi - \varkappa^2\varphi = e\,(z-1)\,\delta\,(\mathbf{r}) + e\varkappa_1^2 e^{-\varkappa_1 r}/r. \qquad (65)$$

We do not know the exact boundary condition at zero but, neglecting the dimension of the "atom," we stipulate that at small distances, after subtracting the self-energy of the particles, φ must be finite and proportional to $z-1$. Then a particular solution of (65) with the second term in the right half yields

$$\varphi \approx -\mathrm{const}\cdot(z-1)\,e\varkappa\,(v_T/v_0)^2.$$

Therefore the addition to the energy of the charge $z-1$ has the form

$$\delta E \approx -\mathrm{const}\cdot(z-1)^2\,e^2\varkappa\,(v_T/v_0)^2. \qquad (66)$$

Multiplying (66) by the density of the "atoms," we obtain an expression of the same form as the last term in formula (59). This classical consideration is undoubtedly crude in view of the difficulty of formulating the problem in this form with any degree of accuracy. However, the presence of the effect of retardation of the interaction of the fast particle relative to the velocity of sound in the plasma (v_T), and the absence of the effect for hydrogen atoms follows apparently even from such a crude model.

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