Ion-atom interaction in the quasiclassical approximation

M. I. Chibisov

I. V. Kurchatov Institute of Atomic Energy
(Submitted December 26, 1974)
Zh. Eksp. Teor. Fiz. **69**, 457–466 (August 1975)

A new method is proposed for constructing, throughout the entire volume, the correct zeroth-approximation wave function in the two-center problem at large distances between centers. This function is used to calculate the exponential part of the asymptotic interaction of the atom with a foreign ion having no core electrons (proton, α particle, etc). This interaction is determined by the exponentially low probability of the sojourn of the electron near the perturbing nucleus. Using particular examples, this interaction is compared with the polarization interaction and it turns out that even for such strongly-polarizing atoms as those of alkali metals the two interactions are approximately the same at intermediate internuclear distances. The calculated interactions lie in the range of thermal and epithermal energies.

PACS numbers: 34.20.Fi

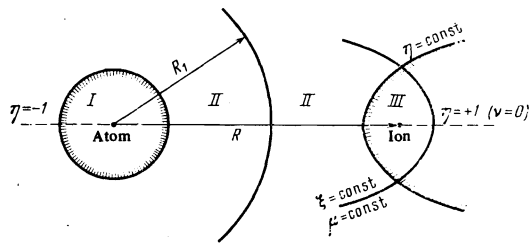
1. The interaction energy of any two atomic particles at large distances R between their nuclei is a sum of two types of interaction: dispersion interaction of a charge with a multipole (or a multipole with a multipole), which is given by a pure power-law series, and an exponential interaction connected with the fact that the probability of finding the atomic electron at any large distance from the atom is finite. The dispersion interaction is determined by the intra-atomic region of the electron coordinates, in which the mutual influence of the atoms is small. This part of the interaction has by now been almost completely investigated and we assume it to be known.

The exponential part of the interaction is determined by the region of the coordinates of the electron near the perturbing particle and cannot be determined by perturbation theory, inasmuch as its influence on the atomic wave function at the location of the perturbing particle is not small. The dispersion interaction at sufficiently large distances between atoms becomes larger than the exponential one, but these distances, as we shall show, are so large that the absolute value of the total interaction turns out to be small here even in the scale of thermal energies.

In this article we calculate the asymptotic form of the exponential part of the interaction of an atomic particle with a completely stripped foreign ion. The atomic particle can be a positive or negative ion, or else a neutral atom. We consider the nonresonant case when the binding energy of the atomic electron does not coincide with the energy of any of the bound states of the electron with the perturbing ion, so that the wave function of the electron is exponentially small near the perturbing ion.

2. Since the probability of observing simultaneously several electrons far from the atom decreases more strongly with increasing distance, the principal contribution to the exponential part of the interaction will come from the succeeding transfer of the atomic electrons to the ion. We then deal in fact with a one-electron problem.

To determine the wave function in the region of the ion, we break up the space of the electron coordinates into three regions—see the figure. We construct the wave function in these regions by going in succession from I to II and III and by matching on the boundaries. We assume that in region I the wave function is close to the unperturbed function in the absence of the ion.



Subdivision of the space of the electronic coordinates into regions: I—region of main concentration of the electron density, II—quasiclassical region, III—region near the perturbing ion, where the quasiclassical approximation is violated.

Separating the unscreened charge-charge interaction from the total energy E, we write down the Schrödinger equation for the electron wave function ψ in the form

$$\left(-\frac{\Delta}{2}-V_1(r_1)-\frac{Z_1}{r_1}+W-E\right)\psi=0,$$
$$E=\bar{E}-\frac{Z_2(Z_1-1)}{R},\quad W=Z_2\left(\frac{1}{R}-\frac{1}{|\mathbf{r}_1-\mathbf{R}|}\right). \tag{1}$$

Here V_1 is the non-Coulomb core on the atom, r_1 is the distance of the electron from the atom; Z_1 and Z_2 are the respective charges of the atomic remainder and the ion. We use the system of atomic units: $e = m = \hbar = 1$. The wave function ψ_1 of the initial state satisfies Eq. (1) with $W = 0$ and $E = E_1$. Its asymptotic form is equal to

$$\psi_1=Q(r_1)Y_{lm}(\theta,\varphi),\quad Q=ar_1^{Z_1n-1}e^{-r_1/n},\quad n=(2|E_1|)^{-1/2}. \tag{2}$$

Here $Y_{lm}(\theta, \varphi)$ is the angular part and Q is the radial part of the unperturbed function; the amplitude a is determined by matching (2) to the numerical wave functions. The quantity a depends on the angular momentum of the removed electron, and also on the total angular momentum of the atomic shell.

3. We determine first the wave function ψ in region II, where the interaction of the electron with the nuclei is smaller than its total energy E and where the quasiclassical approximation is valid. We introduce a new function χ and obtain for it the equation:

$$\psi=\psi_1\chi,$$
$$\left[-\frac{\Delta}{2}-\frac{\nabla\psi_1}{\psi_1}\nabla+W-(E-E_1)\right]\chi=0. \tag{3}$$

We expand Eq. (3) in powers of R^{-1} (but not in powers of r_1/R) in the region $r_1 \sim R$. The zeroth approximation is obtained from (3) by discarding the Laplacian

Copyright © 1976 American Institute of Physics

(the action of which on χ leads to the appearance of terms of next order of smallness in R^{-1}) and the difference $E - E_1$, which is of the order of R^{-4}. In the scalar product of the gradients of the functions ψ_1 and χ it is necessary to retain only the gradient of χ in the direction of the strongest (exponential) damping of ψ_1 along the radius r_1. We then obtain for the quasiclassical factor χ the equation

$$\frac{1}{n}\frac{\partial \chi}{\partial r_1} + W\chi = 0, \quad \chi|_{r_1 \to 0} \to 1. \tag{4}$$

The boundary condition is based here on the fact that near the atom there is a region $1 \ll r_1 \ll R$ where both perturbation theory (for the interaction with the other nucleus) and the quasiclassical approximation are valid: $\psi \to \psi_1$.

Integration of (4) yields

$$\chi = \left[\frac{r_1 - R\cos\theta + |\mathbf{r}_1 - \mathbf{R}|}{R(1-\cos\theta)}\right]^{nZ_2} \exp\left[-nZ_2\frac{r_1}{R}\right]. \tag{5}$$

In elliptic coordinates, this function takes the rather simple form

$$\chi(\xi,\eta) = \left(\frac{1+\xi}{1-\eta}\right)^{nZ_2} \exp\left[-\frac{nZ_2}{2}(\xi+\eta)\right], \qquad \xi = \frac{r_1+r_2}{R}, \quad \eta = \frac{r_1-r_2}{R}, \quad r_2 = |\mathbf{r}_1 - \mathbf{R}|. \tag{6}$$

Expressions (6) and (5) show that the action of the Laplacian on χ does indeed lead to the value $\sim R^{-2}$, whereas in (4) there are retained the terms $\sim R^{-1}$. For a rigorous justification for discarding the Laplacian it is necessary to investigate the expansion of the function χ as $r_1 \to 0$. This expansion is

$$\chi\left(\frac{r_1}{R} \to 0\right) \approx 1 + \frac{nZ_2}{2}\left(\frac{r_1}{R}\right) P_1(\cos\theta) + \frac{nZ_2}{3}\left(\frac{r_1}{R}\right)^2 P_2(\cos\theta) + \frac{nZ_2}{4}\left(\frac{r_1}{R}\right)^3 \left[P_3(\cos\theta) + \frac{nZ_2}{2} P_1(\cos\theta)\right] + \ldots \tag{7}$$

If this expansion were to contain a linear term r_1/R, then the result of the action of the Laplacian on χ would diverge as $r_1 \to 0$. The linear term was eliminated by separating the unscreened nuclear part of the interaction from the total energy.

The factor χ ensures the correct pre-exponential degree of r_1 of the complete function at $r_1 \gg R$, namely $r_1^{n(Z_1+Z_2)-1}$. On the axis between the nuclei the function χ is equal to

$$\chi \approx \left(\frac{R}{R-r_1}\right)^{nZ_2} e^{-nZ_2 r_1/R} \quad (r_1 < R, \theta = 0), \tag{8}$$

which agrees with the result obtained by arbitrarily separating the variables in elliptic coordinates[1] near the internuclear axis. The problem of finding the function ψ in the entire volume is not separable in terms of these coordinates, owing to the presence of non-Coulomb cores and to the boundary condition $\psi|_{r_1 \to 0} \sim \psi_1$, since ψ_1 cannot be represented in the form of a product of a function of ξ by a function of η. This form, as follows from (6), is possessed only by the function χ, which is determined by the asymptotic pure-Coulomb part of the potential energy.

4. The quasiclassical solution (6) diverges in region III as $\eta \to 1$. In this region, the approximate equation (4) is not valid. On the boundary of this region, the solution (6) must be matched to the solution of Eq. (1) or (3), from which it is necessary to separate in the considered approximation all the quantities of order of or smaller than R^{-1} (i.e., to retain the quantities ~ 1), and in which, of course, it is now impossible to discard the Laplacian. Then Eq. (1) reduces simply to the Schrödinger equation for an isolated second nucleus with an electron at a given energy $E = E_1$ and given boundary conditions for the wave function. This function should be matched to ψ at $\eta \to 1$ and $R(1-\eta) \gg 1$ (in this region, near the second nucleus, there are applicable simultaneously both the quasiclassical approximation and perturbation theory with respect to interaction with the first nucleus).

The expansion of (6) near the second nucleus takes the form

$$\chi \approx \left(\frac{2R}{e}\right)^{nZ_2} \nu^{-nZ_2}, \quad 1 \ll \nu \ll R \quad (e = 2.718\ldots). \tag{9}$$

$$\nu = R(1-\eta) = r_2(1 - \cos\sphericalangle r_2, R), \quad \mu = r_2(1 + \cos\sphericalangle r_2, R).$$

We expand in the same manner the unperturbed wave function ψ_1 near the second nucleus. It is necessary to expand the exponential component of the radial part Q:

$$e^{-r/n} \approx \exp\left[-\frac{R}{n} - \frac{\mu-\nu}{2n} - \frac{\mu\nu}{2nR} - \frac{\mu\nu(\mu-\nu)}{4nR^2} + \ldots\right] \tag{10}$$

and the normalized angular part Y:

$$Y_{lm} \approx B_{ml} R^{-m} (\mu\nu)^{m/2} \approx B_{ml}[(\xi-1)(1-\eta)]^{m/2}, \qquad B_{ml}^2 = \frac{(2l+1)(l+m)!}{2^{2m+1}(m!)^2(l-m)!}. \tag{11}$$

We then find that in the matching region $1 \ll \nu \ll R$ the total wave function is represented in a form that is separable in the parabolic coordinates μ and ν:

$$\psi \approx D(n,R) f_1(\mu) f_2(\nu), \quad D = \left(\frac{2R}{e}\right)^{nZ_2} B_{ml} R^{-m} Q(R), \qquad f_1(\mu) \approx \mu^{m/2} e^{-\mu/2n}, \ \mu \gg 1; \quad f_2 \approx \nu^{m/2 - nZ_2} e^{\nu/2n}, \ \nu \gg 1. \tag{12}$$

In all the foregoing formulas, m stands for the absolute value of the projection of the angular momentum. The Schrödinger equation in the Coulomb field of the second nucleus is separable in the parabolic coordinates[2]:

$$\frac{d}{d\mu}\mu\frac{df_1}{d\mu} + \left[-\frac{\mu}{4n^2} + \beta_1 - \frac{m^2}{4\mu}\right] f_1 = 0,$$
$$\frac{d}{d\nu}\nu\frac{df_2}{d\nu} + \left[-\frac{\nu}{4n^2} + \beta_2 - \frac{m^2}{4\nu}\right] f_2 = 0, \quad \beta_1 + \beta_2 = Z_2. \tag{13}$$

The region where the quasiclassical approximation is violated near the second nucleus is inside the paraboloid $R \gg \nu = \text{const} \gg 1$, since the introduced elliptic and parabolic coordinates coincide in this region. This means that in this entire region the dependence of ψ on μ coincides with the asymptotic form of $f_1(\mu)$ in (12). Substituting this expression for $f_1(\mu)$ in the first equation of (13), we obtain the separation constants $\beta_{1,2}$. Then the solution of the second equation, which is finite at zero and takes the asymptotic form (12), is the function

$$f_2(\nu) = n^{-nZ_2}\frac{\Gamma(m+1-nZ_2)}{\Gamma(m+1)}\nu^{m/2}e^{-\nu/2n}F\left(m+1-nZ_2;\ m+1;\ \frac{\nu}{n}\right). \tag{14}$$

Here $F(\ldots)$ is a confluent hypergeometric function.[2] Using again elliptic coordinates, we can write down the complete wave function in the form

$$\psi = \psi_1\chi, \qquad \chi = (1+\xi)^{nZ_2}e^{-nZ_2\xi/2} \times \begin{cases} (1-\eta)^{-nZ_2}e^{-nZ_2\eta/2}, & \eta \leqslant \eta_1 \\ e^{-nZ_2/2}\left(\frac{R}{n}\right)^{nZ_2}\frac{\Gamma(m+1-nZ_2)}{\Gamma(m+1)}e^{-R(1-\eta)/n}F\left(m+1-nZ_2;\ m+1;\ \frac{R(1-\eta)}{n}\right), & \eta_1 \leqslant \eta \leqslant 1. \end{cases} \tag{15}$$
$$1-\eta_1 \ll 1, \quad R(1-\eta_1) \gg 1.$$

At the value $\eta = \eta_1$, the quasiclassical solution is matched with the function (14).

The solution constructed near the second nucleus increases exponentially in the direction towards the first nucleus, so that the fact that it is finite at $\eta = 0$ does not determine the energy. This solution has parabolic symmetry and is analogous, for the case $m = 0$, to the solution for the positive energies with a plane wave at infinity.[2] For the case of two pure Coulomb centers, when the problem is strictly separable in elliptic coordinates, this solution was obtained earlier by Gershteĭn and Krivchenkov.[3] The function (15) for this particular case coincides with the function obtained in[3] (for noninteger Z_1/Z_2).

We note that the function (15) is orthogonal (as it should be) to the functions of all the ion states with energies lower than E_1 (and identically in E_1), as can be verified by direct calculation.

The function (14) for integer and negative $m + 1 - nZ_2$ becomes infinite, and these values of nZ_2 correspond to the eigenvalues of the energy at the second nucleus. We have no right to consider a purely resonant situation, for in this case the solution (15) cannot be constructed, inasmuch as at resonance a solution that is finite in the second nucleus has no component that diverges at infinity. In order to be able to match together both parts of the function χ in (15), it is necessary that the damped solution with resonant amplitude at $\eta = \eta_1$ be much smaller than the nonresonant diverging solution. Using the asymptotic expressions for both solutions[2], we obtain the condition for the existence of the solution (15):

$$\frac{\Gamma(m+1-nZ_2)}{\Gamma(m+1)}\left(\frac{R\eta_1}{n}\right)^{2nZ_1-1-m}\exp\left(-\frac{R\eta_1}{n}\right)\ll 1. \qquad (15a)$$

Since the small quantity η_1 does not depend on R, this condition can, generally speaking, be satisfied, with increasing R, for an arbitrarily small resonance defect.

5. To calculate the shift of the system energy from its value at $R \to \infty$, we multiply (1) by ψ_1, multiply the equation for ψ_1 by ψ, and then subtract one from the other and integrate over a spherical volume Ω whose center is at the nucleus of the atom and whose radius is $R_1 \sim R$. We then obtain (S is the surface of the sphere):

$$(E-E_1)\int_\Omega \psi\psi_1\,d\tau = \int_\Omega W\psi\psi_1\,d\tau - \frac{1}{2}\oint_S(\psi_1\nabla\psi-\psi\nabla\psi_1)\,dS. \qquad (16)$$

The volume integral on the left in (16) is close to unity, accurate to quantities of order R^{-4}, as can be seen from the expansion (7).

We shall show that the quasiclassical region, where Eq. (4) is valid, cannot make a contribution to the sought exponential part in the considered approximation. We choose $R_1 < R$ (e.g., R/2), Using spherical coordinates with center at the first nucleus, and integrating once by parts in the volume integral on the right side of (16), we obtain

$$E-E_1 = \frac{n}{2}\int_0^{R_1} e^{-2r_1/n}\,de^{2r_1/n}r_1^2Q^2(r_1)\int_0^{4\pi} Y_{lm}^2 W\chi\,d\Omega$$
$$-\frac{n}{2}R_1^2Q^2(R_1)\int_0^{4\pi} Y_{lm}^2\left[\frac{1}{n}\frac{\partial\chi}{\partial r_1}+W\chi\right]_{r_1=R}d\Omega. \qquad (17)$$

If $R_1 < R$, then the integration sphere does not intersect the region where the quasiclassical approximation is violated, and the surface integral vanishes here by virtue of Eq. (4). The volume integral then yields quantities of the next order of smallness in R^{-1} since the functions under the differentiation sign have a power-law behavior and their gradients are proportional to R^{-1}. If we put $R = R_1$, then a contribution from the nonquasiclassical region, in which the derivative function χ is of the order of unity, appears in both the surface and in the volume integral.

6. We let the radius of the sphere S in (16) go to infinity, so that the surface integral vanishes. We calculate the volume integral due to the perturbation of W in elliptic coordinates, using the function (15). We employ the procedure of integrating by parts. Integration of the exponential part of the wave function and differentiation of the remaining integrand with respect to the variable η yields the expansion of the energy in the reciprocal powers R^{-1}. Since the function (15) is only the principal term of the expansion, it suffices to integrate m times with respect to ξ. The dependence of the wave function on the variable η is of different kind, namely, the function χ near the ion has a structure with a gradient (with respect to the variable η) on the order of R (the derivative of this function with respect to the usual variable $\mathbf{r}_2 = \mathbf{r}_1 - \mathbf{R}$, which is the distance from the nucleus of the ion, is of the order of unity). Consequently, in order to determine the principal term of the expansion of the contribution to the energy from the region near the nucleus of the ion in powers of R^{-1} it is necessary to integrate with respect to η by parts an infinite number of times.

Substituting (15) in (16) and integrating m times by parts with respect to ξ, we get (after changing from η to the variable ν):

$$E-E_1 = \frac{Z_2n^{m+1}}{2}m!B_{ml}^2R^{-2m}Q^2(R)\int_{2R}^{0} e^{\nu/n}\nu^m\chi(\nu,\xi=1)\,d\nu. \qquad (18)$$

Integrating here by parts an infinite number of times, we obtain the sought contribution of the upper limit ($\nu = 0$):

$$E-E_1 = \frac{Z_2}{2}\left(\frac{2}{e}\right)^{nZ_2}n^{2m+2-nZ_2}\Gamma(m+1-nZ_2)B_{ml}^2R^{nZ_2-2m}Q^2(R)I_m(nZ_2),$$
$$I_m(nZ_2) = \sum_{k=0}\left[\frac{d^k}{dx^k}x^me^{-x}F(m+1-nZ_2;\,m+1;\,x)\right]_{x=0}. \qquad (19)$$

Integration by parts in (18) generates at the lower limit ($\nu = 2R$) the power-law series of the dispersion part of the interaction. This can be seen after substituting in (18) the expansion (7). However, the quasiclassical accuracy with which the expansion (7) is determined is not sufficient for an exact determination of the coefficients of the dispersion series—the induced multipole moments. To calculate them it is necessary to obtain more accurately the solution for χ in region I, and this exact solution differs from the expansion (7) in the presence of quantities $\sim r^kR^{-p}$, where $k < p$. This method of calculating the polarizability of the ground state of the hydrogen atom was used, for example, by Dalgarno and Lewis.[4] Comparing for this particular case the expression obtained for χ in[4] with the expansion (7), we find that their principal terms coincide.

The infinite sum in (19) was calculated in the Appendix. Using (A.8), we write down the final result in the form

$$E-E_1 = A(n,\,m,\,Z_2)R^{n(2Z_1+Z_2)-2m-2}e^{-2R/n},$$
$$A = N_{ml}\frac{Z_2}{4}\frac{a^2n^{2m+2}}{(ne)^{nZ_2}}\frac{(2l+1)\,(l+m)!}{2^{2m}(m)!\,(l-m)!}\Gamma(m+1-nZ_2). \qquad (20)$$

We have introduced here the number N_{ml} of the electrons in the atomic shell with given quantum numbers l and m; this number can be either 1 or 2 for different atoms. It takes into account the contribution made to (16) by the equivalent electrons of the atom. If an atomic shell with given l contains electrons with different m, then the largest interaction is given by electrons with m = 9, and in this case inclusion of the interaction of the electrons with $m \neq 0$ is an exaggeration of the accuracy. The decrease of the power of R in (20) with increasing m is due to the vanishing, on the entire internuclear axis, of both functions ψ and ψ_1 at $m > 0$ (the projection of the angular momentum is a rigorous integral for both states). Compared with the square of the unperturbed function, formula (20) contains an additional power R^{nZ_2} due to the long-range character of the Coulomb field of the perturbing ion.

The constant A in (20) can be either positive or negative. The energy shift then corresponds either to repulsion or attraction between the nuclei. According to (16), the energy shift is linear in ψ (and not quadratic), and depends on its sign in the region of the second nucleus. The exact results (20) shows that A has the same sign as ψ at the location of the second nucleus. Since the boundary conditions for ψ are specified at $r_2 \to \infty$, the sign of $\psi(R)$ varies with n. We fix the quantities R and n and vary the perturbing field, i.e., the value of Z_2. At sufficiently small Z_2, all the energy levels of the electron on the second nucleus lie higher than E_1. In this case the wave function near the second nucleus has no nodal surfaces. Consequently it has in this region the same sign as ψ_1 (more accurately, the asymptotic part (4)), and we obtain $A > 0$ and repulsion in (20). With increasing Z_2, when one level turns out to be lower than E_1 for the perturbing ion, then one nodal surface appears for ψ; near the second nucleus, the sign of ψ is opposite the sign of ψ_1, and we get $A < 0$ and attraction, etc. The sign of the interaction (20) thus depends on the number of energy levels located below E_1, for the second nucleus with given value of m. The pole gamma-function in (20) accounts for this alternation of the sign of the constant A for a pure Coulomb perturbing field, and A decreases rapidly with increasing nZ_2. It must be recalled here that we are not considering a resonant situation, i.e., the calculated shift should be small in comparison with the distance to the levels closest to E_1.

7. The interaction (20) assumes the greatest role for a case close to resonance, for in this case the constant A is the largest. The condition (15a), however, restricts us to consideration of interactions $E - E_1$ much smaller than the resonance defect δE. The total interaction—including the polarization interaction—takes the form

$$E-E_1=AR^{n(2Z_1+Z_2)-2m-2}e^{-2R/n}-\alpha R^{-4}/2. \qquad (21)$$

We present a few examples.

1) The pair Ar + H^+. The parameter values are $l = 1$, m = 0, N = 2, a = 2.7, $\alpha = 11$, n = 0.93, $\delta E = 0.08$ at. un. We obtain

$$E-E_1=55.3\,R^{0.79}e^{-2.15R}-5.5\,R^{-4}.$$

There is a well of depth ~0.1 eV at $R \sim 5.5$.

2) The pair Kr + H^+. The parameters are $l = 1$, m = 0, N = 2, a = 2.75, $\alpha = 16.8$, n = 0.986, $\delta E = 0.015$ at. un. and

$$E-E_1=296\,R^{0.98}e^{-2.03R}-8.4\,R^{-4}.$$

3) The pair Cs + H^+. The parameter values are $l = m = 0$, N = 1, a = 0.416, $\alpha = 360$, n = 1.87 and we obtain

$$E-E_1=-0.06\,R^{3.61}e^{-1.07R}-180\,R^{-4}.$$

Both terms are negative and become equal at $R \sim 7$ at. un. The values of the polarizability α and of the amplitude a were taken from the book[5].

In conclusion, the author is deeply grateful to M. A. Leontovich and O. B. Firsov for a discussion of the problems touched upon here.

APPENDIX

The sum (19) contains under the derivative sign a function for which the series in positive powers begins with x^m. Therefore the derivatives of order higher than k = m do not vanish at the point x = 0. We consequently have

$$I_m(nZ_2)=\sum_{k=m}^{\infty}\frac{d^k}{dx^k}[x^m e^{-x}F(m+1-nZ_2;\,m+1;\,x)]_{x=0}. \qquad (A.1)$$

Using relation (d.10) and the contour integral (d.8) of[2] for F, we get

$$x^m e^{-x}F(m+1-nZ_2;\,m+1;\,x)=\frac{\Gamma(m+1)}{2\pi i}\int_C e^{x\tau}(\tau+1)^{-nZ_2}\tau^{nZ_2-m-1}\,d\tau. \qquad (A.2)$$

The contour C is a loop that goes counterclockwise around the cut between the points $\tau = 0$ and $\tau = -1$ (the sum of the powers in the integral (A.2) is an integer). Differentiating (A.2) we obtain

$$\frac{d^k}{dx^k}x^m e^{-x}F(m+1-nZ_2;\,m+1;\,x)=\frac{\Gamma(m+1)}{2\pi i}\int_C e^{x\tau}(\tau+1)^{-nZ_2}\tau^{k-m+nZ_2-1}\,d\tau. \qquad (A.3)$$

Substituting (A.3) in (A.1), we obtain

$$I_m(nZ_2)=\frac{\Gamma(m+1)}{2\pi i}\int_C(\tau+1)^{-nZ_2}\tau^{nZ_2-1}\left(\sum_{l=0}^{\infty}\tau^l\right)d\tau. \qquad (A.4)$$

We can deform the contour C in such a way as to satisfy the condition for the existence of a sum of an infinitely decreasing geometric progression

$$\sum_{l=0}^{\infty}\tau^l=\frac{1}{1-\tau},\quad |\tau|<1,\quad \mathrm{Re}\,\tau<0. \qquad (A.5)$$

This condition, generally speaking is violated on the contour near $\tau = -1$. By differentiating k times by parts we can always make the power $(\tau+1)^{-nZ_2+k}$ integrable at the limit $\tau = -1$, after which the contour C can be drawn directly through the point $\tau = -1$ in such a way that the series (A.5) converges on the entire contour. We can therefore substitute (A.5) in (A.4) for all nZ_2:

$$I_m(nZ_2)=\frac{\Gamma(m+1)}{2\pi i}\int_C(\tau+1)^{-nZ_2}\tau^{nZ_2-1}(1-\tau)^{-1}\,d\tau; \qquad (A.6)$$

C goes around the cut between $\tau = 0$ and $\tau = -1$ counterclockwise. By making the substitution $\tau = -1 + t$ we reduce this integral to the integral (e.3) of[2] for the complete hypergeometric function:

$$I_m(nZ_2)=-\frac{\Gamma(m+1)}{4\pi i}\int_C(-t)^{-nZ_2}(1-t)^{nZ_2-1}\left(1-\frac{t}{2}\right)^{-1}dt$$
$$=\frac{1}{2}\Gamma(m+1)F(1-nZ_2;\,1;\,1;\,1/2). \qquad (A.7)$$

With the aid of relation (e.4) of[2] we obtain for the functions F

$$I_m(nZ_2)=\frac{\Gamma(m+1)}{2}\left(\frac{1}{2}\right)^{nZ_2-1}F(nZ_2;\ 0;\ 1;\ {}^1/_2)=2^{-nZ_2}\Gamma(m+1). \quad \text{(A.8)}$$

There is also another proof of (A.8), and is convenient for an explanation of the connection between the general result and perturbation theory as $nZ_2 \to 0$. Using relation (d.10) of[2], we can rewrite (A.1) in the form

$$I_m(nZ_2)=\Gamma(m+1)\sum_{l=0}^{\infty}\frac{(m+1)(m+2)\dots(m+l)}{\Gamma(l+1)}\frac{d^l}{dx_l}F(nZ_2;\ m+1;\ -x)\Big|_{x=0}. \quad \text{(A.9)}$$

Differentiating the series representation of F in positive powers of x, we obtain the series

$$I_m(nZ_2)=\Gamma(m+1)\sum_{l=0}^{\infty}(-1)^l\frac{\Gamma(nZ_2+l)}{\Gamma(nZ_2)\Gamma(l+1)}. \quad \text{(A.10)}$$

This series converges when the positive and negative terms are pairwise combined at $nZ_2 < 1$. In the convergence region, it can be regarded as the limit of the series

$$I_m(nZ_2)=\Gamma(m+1)\lim_{x\to -1+0}\left[1+\frac{nZ_2\cdot 1!}{1!}\frac{x}{1!}+\frac{nZ_2(nZ_2+1)\cdot 2!}{2!}\frac{x^2}{2!}+\dots\right], \quad \text{(A.11)}$$

which represents the complete hypergeometric function $F(nZ_2; 1; 1; x)$. Using relation (e.5) of[2] for these functions, we obtain (A.8). The function (A.8) can be regarded as an analytic continuation of the series (A.10) to include all values of nZ_2. Then the requirement that $I_m(nZ_2)$ be analytic leads to the result (A.8) for all nZ_2. In the derivation given at the start of the Appendix, the analyticity of $I_m(nZ_2)$ was a corollary.

As $nZ_2 \to 0$, the principal term of the expansion (A.8)

$$I_m(nZ_2)\to\Gamma(m+1)[1-nZ_2\ln 2+\dots],\quad nZ_2\to 0 \quad \text{(A.12)}$$

coincides with the zeroth term of the series (A.9), i.e., it is given by the value of the function ψ at the point of location of the second nucleus (for m = 0). The next term, on the other hand, which is proportional to nZ_2, is contained in all the terms of the series (A.10), i.e., in all the derivatives of the function χ at the location of the second nucleus. This contribution can be easily separated from the series (A.10):

$$I_m(nZ_2)\to\Gamma(m+1)\left[1-nZ_2\sum_{l=1}^{\infty}\frac{(-1)^l}{l}\right]=\Gamma(m+1)[1-nZ_2\ln 2+\dots], \quad nZ_2\to 0, \quad \text{(A.13)}$$

in accord with (A.11). This singularity of the series is connected with the following singularity of the complete function ψ at the location of the second nucleus. Although $\chi \to 1$ as $n \to 0$ and at fixed Z_2, all its derivatives with respect to ν at diverge $\nu = 0$ (starting with the second derivative), as is seen from (A.10) (on the other hand, the derivatives with respect to $x = \nu/n$, which are contained in (18), are finite). The first derivative with respect to ν is equal to $-Z_2$. If Z_2 is made to approach zero at fixed n, then $\psi \to \psi_1$ without singularities.

[1] B. M. Smirnov, Zh. Eksp. Teor. Fiz. 46, 1017 (1964); 47, 518 (1964) [Sov. Phys.-JETP 19, 692 (1964); 20, 345 (1965)].

[2] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics) Gostekhizdat, 1963 [Addison-Wesley, 1965].

[3] S. A. Gershtein and V. D. Kryvchenko, Zh. Eksp. Teor. Fiz. 40, 1491 (1961) [Sov. Phys.-JETP 13, 1044 (1961)].

[4] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. A233, 70 (1955).

[5] B. M. Smirnov, Atomnye stolknoveniya i élementarnye protsessy v plazme, (Atomic Collisions and Elementary Processes in Plasma) Atomizdat, 1968.

Translated by J. G. Adashko
48