ON THE THEORY OF NEGATIVE ION FORMATION IN SLOW ATOMIC COLLISIONS

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Nonstationary perturbations acting on an electron and leading at a certain time instant to the appearance of a bound s state are considered. The capture probability and the momentum distribution in the continuous spectrum are determined in the adiabatic approximation. A relation between this problem and the formation of negative ions in slow collisions is demonstrated.

IN the present paper we consider the triple collision between a monochromatic electron and two neutral atoms. The deBroglie wavelength of the electron is assumed to be much larger than the atomic dimensions, and the velocities of the atoms are regarded as small compared with the velocity of the electron. Such a collision either leads to the formation of a negative ion, or else the electron remains in a state of the continuous spectrum but gets "smeared out" in the energy. If the colliding atoms are different and the electron is sufficiently slow, this problem can be solved within the framework of a spherically symmetric model, by replacing the colliding atoms by a narrow potential well with variable parameters. Indeed, the instantaneous terms $E_0(R)$ and $E_1(R)$ of a weakly bound electron in the field of two neutral atoms are given by the following equations[1] ($\hbar = m = 1$):

$$k_0 = \frac{\varkappa_a + \varkappa_b}{2} - \left[\left(\frac{\varkappa_a - \varkappa_b}{2}\right)^2 + \frac{\exp(-2k_0R)}{R^2}\right]^{1/2},$$

$$k_1 = \frac{\varkappa_a + \varkappa_b}{2} + \left[\left(\frac{\varkappa_a - \varkappa_b}{2}\right)^2 + \frac{\exp(-2k_1R)}{R^2}\right]^{1/2}. \quad (1)$$

Here $k_{0,1}^2 \equiv -2E_{0,1}$, $\kappa_{a,b}^2 \equiv -2E_{a,b}$, where $E_{a,b}$ is the binding energy of the negative ion formed by the atom a and b, respectively; R is the distance between the atoms. It is seen from (1) that the upper term $E_0(R)$ merges with the continuous spectrum for $R = R_0 \equiv (\kappa_a\kappa_b)^{-1/2}$. It is clear that it is this point which is most important in the capture of the electron into a bound state. Since the energy $E_1(R)$ does not become anomalously small for any R, the absorption goes mainly into the term E_0. Thus the formation of the negative ion with the lowest energy is the most probable. We shall assume that the momentum of the electron k is much smaller than min (κ_a, κ_b). Then the deBroglie wavelength of the electron is much larger than the distance between the atoms in the region most important for the capture. Hence the perturbing potential is localized near the origin in a region which is small compared with the wavelength of the electron. Therefore the s wave will predominate in the ground state wave function, since the higher spherical functions vanish at the origin and cannot interact effectively with the perturbation.

Let us now discuss the character of the wave function of the final state (bound electron) near the transition point.

The function corresponding to the term E_0 has the form

$$\psi(\mathbf{r}) = \text{const}\cdot\left[\frac{\exp(-k_0r_a)}{r_a} + \frac{\exp(-k_0R - k_0r_b)}{R(k_0 - \varkappa_b)r_b}\right],$$

$$r_a = \left|\mathbf{r} - \frac{\mathbf{R}}{2}\right|, \quad r_b = \left|\mathbf{r} + \frac{\mathbf{R}}{2}\right|.$$

At the transition point we have $R = (\kappa_a, \kappa_b)^{-1/2}$ and $k_0(t) \to 0$, therefore the wave function has the form

$$\psi(\mathbf{r}) \sim \left(\frac{\sqrt{\varkappa_b}}{|\mathbf{r} - \mathbf{R}/2|} - \frac{\sqrt{\varkappa_a}}{|\mathbf{r} + \mathbf{R}/2|}\right).$$

We shall, however, keep in mind that $\psi(\mathbf{r})$ decays exponentially for values of $R \gtrsim 1/k_0$. Let us expand $\psi(\mathbf{r})$ in terms of Legendre polynomials and estimate the importance of the different spherical harmonics:

$$\psi(\mathbf{r}) = \psi_s(r)P_0(\cos\theta) + \psi_p(r)P_1(\cos\theta) + \ldots$$

After simple calculations we obtain

$$\psi_s \sim (\sqrt{\varkappa_a} - \sqrt{\varkappa_b})\begin{cases} 2/R_0 & \text{for } r < R_0/2 \\ 1/r & \text{for } r > R_0/2. \end{cases}$$

(Since we only want order-of-magnitude estimates, we omit the numerical coefficients.) Let us estimate the contribution of the s wave to the full norm of the function ψ and take into account the fact that the integral $\int|\psi_s|^2r^2dr$ must be cut off for $r \sim k_0^{-1}$. Since in this region $k_0R_0 \ll 1$, we find

$$\int |\psi_s|^2r^2dr \sim (\sqrt{\varkappa_a}-\sqrt{\varkappa_b})^2/k_0. \qquad (2)$$

Analogous calculations for $\psi_p(r)$ lead to the result

$$\psi_p(r) \sim (\sqrt{\varkappa_a}+\sqrt{\varkappa_b}) \begin{cases} 8r/R_0^2 & \text{for } r < R_0/2 \\ R_0/r^2 & \text{for } r > R_0/2 \end{cases}$$

The corresponding normalization integral converges even without cut-off, and we obtain

$$\int |\psi_p|^2r^2dr \sim (\sqrt{\varkappa_a}+\sqrt{\varkappa_b})^2R_0. \qquad (3)$$

If

$$R_0k_0(R) \ll \left(\frac{\sqrt{\varkappa_a}-\sqrt{\varkappa_b}}{\sqrt{\varkappa_a}+\sqrt{\varkappa_b}}\right)^2, \qquad (4)$$

in the transition region, then (2) and (3) show that the s wave plays the predominant role in the wave function of the final state. The condition (4) is clearly not fulfilled when the colliding atoms are identical. In the following we shall be concerned with nonidentical atoms. In this case the right-hand side of (4) is in general of order unity, so that the condition (4) is satisfied in the transition region. Outside this region the effect of the higher harmonics increases, but the system develops adiabatically, i.e., the electron remains in the state corresponding to the term $E_0(R)$.

It is clear from what has been said above that the s wave plays the dominant role in the total wave function of the initial and final states. This justifies the use of a spherically symmetric model.

We shall assume that in the initial state, i.e., for $t \to -\infty$, the electron is located in the field of a scattering potential and has the definite energy $E = k^2/2$. The parameters of the potential vary slowly with the time. At $t = 0$ there appears a discrete level $E_0(t) \equiv -k_0^2(t)/2$. For $t = 0$ the level energy $E_0(t)$ vanishes and goes to some constant negative value at $t \to +\infty$. The energy scale is chosen such that the scattering potential vanishes at large distances. Let us assume that the potential has spherical symmetry for all values of t and that the level $E_0(t)$ corresponds to the angular momentum $l = 0$. The initial state of the particle also has vanishing angular momentum. Then the wave function evidently has $l = 0$ for all values of t.

Let us make the requirements on the characteristic parameters of the problem more precise. We denote the time during which the potential changes appreciably by T. It is clear that the sudden approximation is valid if the distance traversed by the particle with momentum k during the time T is much less than the deBroglie wavelength.

Consider now the opposite limiting case: $k^2T \gg 1$. Let us moreover restrict the momentum from above by the condition $ka \ll 1$, where a is a characteristic dimension of the potential well. From these two inequalities we find $T \gg a^2$, which is the adiabaticity condition for the states of the discrete spectrum, since a^{-2} is equal in order of magnitude to the distance between the discrete levels in a well of width a.

As is usually the case in adiabatic problems, only a small neighborhood near the transition point $t = 0$ is of importance. In this region one has $k_0(t) = -\beta t$, where β is a positive constant. [$k_0(t)$ goes linearly to zero for an s state.] From this we obtain an estimate for the transition region $|t| \sim \beta^{-2/3}$. For these values of t we have $k_0(t)a \ll 1$, so that the approximation for resonance scattering of slow particles is valid. Thus the details of the scattering potential are not essential, and its presence is accounted for only by a phase in the asymptotic wave function. It is therefore sufficient to solve the nonstationary Schrödinger equation for a free particle with the boundary condition

$$\frac{\partial}{\partial r}(r\psi(r,t)|_{r=0} = +k_0(t)(r\psi(r,t))|_{r=0} \qquad (5)$$

(the idea for this approach is due to L. P. Pitaevskiĭ).

The "ionization" problem in this approximation has been solved by Demkov.[2] Using his results, we may obtain the probability for the capture of an electron into a discrete level with the help of the principle of detailed balance. However, the energy distribution of the electrons in the continuous spectrum remains unknown. When this distribution is found, the complete S matrix of our problem is determined. In our case the initial condition imposed on the wave function has the form

$$\psi(r, t\to -\infty) = \frac{1}{\sqrt{V}}\frac{\sin(kr+\delta)}{kr}, \qquad (6)$$

where δ is the scattering phase. This corresponds to keeping only the s wave part of the plane wave, normalized to unity in the volume V.

As usual, we introduce the function $\chi(r, t) = r\psi(r, t)$, which satisfies the Schrödinger equation

$$\left(i\frac{\partial}{\partial t}+\frac{1}{2}\frac{\partial^2}{\partial r^2}\right)\chi(r,t) = 0 \qquad (7)$$

and the above-mentioned boundary condition (5).

Following Demkov, we continue the solution to the negative half-axis with even parity and take account of condition (5) by introducing the potential $k_0(t)\delta(x)$:

$$i\frac{\partial\chi}{\partial t}+\frac{1}{2}\frac{\partial^2\chi}{\partial x^2}=k_0(t)\delta(x)\chi. \qquad (8)$$

Using the Green's function of (7), we obtain the following relation between $\chi(x, t)$ and $\chi(0, t)$:

$$\chi(x,t)=\frac{e^{-3\pi i/4}}{\sqrt{2\pi}}\int_{-\infty}^{t}\frac{k_0(t')\chi(t',0)}{\sqrt{t-t'}}e^{ix^2/2(t-t')}dt'$$
$$+\int_{-\infty}^{+\infty}\varphi(p)e^{ipx-ip^2t/2}dp, \qquad (9)$$

where $\varphi(p)$ is an unknown function which is chosen such that the initial condition (6) is fulfilled.

For large negative times $|t| \gg \beta^{-2/3}$ we have $k_0(t) = \bar{k}_0 = \text{const}$. Fixing the time at a value in this region, we find for the Fourier transform of (9) with respect to x

$$\varphi(p)=\alpha k\delta(p^2-k^2), \qquad \alpha\equiv ie^{-i\delta_-}, \qquad (10)$$

where δ_- is the initial scattering phase, $\tan\delta_- = k/k_0$. The linear approximation for $k_0(t)$ is valid in the region $|t| \ll T$, while the integral in (9) starts at $-\infty$. We therefore proceed in the following fashion: we assume that $k_0(t) = \bar{k}_0 = \beta T$ for $t < -T$ and $k_0(t) = -\beta t$ for $t > -T$ ($T \gg \beta^{-2/3}$); the final result will not depend on T. The error incurred in this way is connected with the neighborhood $\Delta t \sim 1/k^2$ of the corner point $t = -T$.

Thus we obtain the following equation for $\chi(0, t)$:

$$\chi(0,t)=\frac{e^{-3\pi i/4}}{\sqrt{2\pi}}\bar{k}_0\int_{-\infty}^{-T}\frac{\sin\delta_- e^{-ik^2t/2}}{\sqrt{t-t'}}dt'$$
$$+\frac{e^{-3\pi i/4}}{\sqrt{2\pi}}\int_{-T}^{t}\frac{(-\beta t')\chi(t',0)}{\sqrt{t-t'}}dt'+\alpha e^{-ik^2t/2}. \qquad (11)$$

The exact solution of (11) can only be obtained if the lower limit in the second integral is $-\infty$. Let us extend this integral to $-\infty$ and neglect the terms

$$\frac{e^{-3\pi i/4}}{\sqrt{2\pi}}\int_{-\infty}^{-T}\frac{\bar{k}_0\sin\delta_- e^{-ik^2t'/2}-(-\beta t')\chi(0,t')}{\sqrt{t-t'}}dt'.$$

By solving the resulting equation

$$\chi(t)=\frac{e^{-3\pi i/4}}{\sqrt{2\pi}}\int_{-\infty}^{t}\frac{(-\beta t')\chi(t')dt'}{\sqrt{t-t'}}+\alpha e^{-ik^2t/2}, \qquad (12)$$

where $\chi(t) \equiv \chi(0, t)$, we estimate the magnitude of the neglected term.

The calculations show that this term is of the order $(k/\beta T)^2$ for values of t far from the corner point $t + T \gg k^{-2}$. We shall assume that $k \ll \beta T$ and keep only terms of first order in this ratio. This last condition implies that the slope of $k_0(t)$ with respect to the time axis must be large for $t = 0$.

In the opposite case, the region where the adiabaticity is violated will not be small compared to the region where the linear approximation for $k_0(t)$ holds. Equation (12) is solved by the Laplace method: $\chi(t) = \int_C Z(u)e^{iut}du$, where Z(u) must satisfy the equation

$$\int_C\left[Z(u)+\frac{i\beta}{\sqrt{2u}}Z'(u)\right]e^{iut}du=\alpha e^{-ik^2t/2} \qquad (13)$$

It can be seen that the solution of (13) is

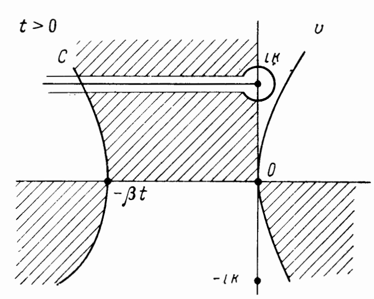
$$\chi(t)=\frac{\alpha k}{(-2\pi i)}\frac{e^{-k^3/3\beta}}{\beta}\int_C\exp\left\{i\frac{v^3}{3\beta}+i\frac{v^2t}{2}\right\}\ln(v^2+k^2)vdv, \qquad (14)$$

where the contour C encloses the logarithmic cut, running from the point ik to infinity in the sector $2\pi/3 < \arg v < \pi$ (cf. the figure). In the dashed region the exponential has a modulus larger than one.

Using (9) we find

$$\chi(x,t)=i\alpha\sin k|x|e^{-ik^2t/2}+\frac{\alpha k}{\beta}\exp\left(-\frac{k^3}{3\beta}\right)\int_{ik}^{ik-\infty}\exp\left\{i\frac{v^3}{3\beta}\right.$$
$$\left.+i\frac{v^2t}{2}+v|x|\right\}vdv. \qquad (15)$$

It is easy to verify that $\chi(x, t)$ satisfies the Schrödinger equation (7), the boundary condition (5), and the initial condition (6) at $t = -T$ with an accuracy up to terms of order $k/\beta T$. This holds only for $x \ll kT$, which is of course a consequence of the causality principle.



Projecting $\chi(x, t)$ for $t \to +\infty$ on the eigenfunctions corresponding to the discrete level and the continuous spectrum, we obtain the capture probability

$$w=\frac{\pi}{\beta V}\exp\left(-\frac{2k^3}{3\beta}\right) \qquad (16)$$

and the momentum distribution in the continuous spectrum

$$\nu(p)=\frac{\pi}{2V}\left[\left(\frac{2}{\pi}V-\frac{4}{\beta}\right)\delta(p-k)\right.$$
$$\left.+\frac{4p^2}{\beta^2}\exp\left\{\frac{2}{3\beta}(p^3-k^3)\right\}\right],$$
$$p<k; \quad \nu(p)=0, \quad p>k. \qquad (17)$$

The vanishing of $\nu(p)$ for $p > k$ is evidently due to a special feature of our model: the δ-function-like well with an amplitude which depends linearly on the time. If we assume that $k_0(t)$ tends to a constant for $t \to +\infty$, we obtain a power-type "tail" $\nu(p) \sim p^{-4}$ for $p \gg k$.

It is seen from (16) that the capture probability is inversely proportional to the volume, since the initial wave function of the electron is a plane wave normalized to unity in the volume V. Let us assume that there are $N = nV$ electrons with momentum k in the volume V. For the capture probability of one of the electrons we easily obtain with the help of combinatorial theory:

$$W = 1 - (1 - w)^{nV} = 1 - \exp\left[-\frac{\pi n}{\beta} e^{-2k^3/3\beta}\right]. \quad (18)$$

However, we must restrict ourselves to small values of n/β, since the problem has been solved without account of the Pauli principle. On the other hand, the captured electrons are effectively characterized by such values of the deBroglie wavelength $\lambda \sim \beta^{-1/3}$ that the average distance between the particles becomes comparable to λ precisely when $n \sim \beta$. Thus we must expand (18):

$$W = \frac{\pi n}{\beta} \exp\left(-\frac{2k^3}{3\beta}\right). \quad (19)$$

In the same way the explicit dependence on V is eliminated from (17). The order of magnitude of the quantity β is estimated in the following way:

$$\beta = \left(\frac{dk_0}{dt}\right) = \left[\frac{dk_0}{dR} v(R)\right]_{R=R_0},$$

where v(R) is the radial velocity of the atoms, and R_0 is the root of the equation $k_0(R) = 0$. From this we obtain $\beta \sim a_i^{-3} v(R_0)/v_e$. Here a_i is of the order of the radius of the negative ion, and v_e is the orbital velocity of the "extra" electron.

During one collision the critical point $R = R_0$ is passed through twice. As the atoms approach each other, the inclination of the term $k_0(t)$ corresponds to the transition of the discrete level into the continuous spectrum. Therefore the passing through this point leads only to a smearing-out of the momenta of the electrons. In this case the problem leads again to Eq. (12) with the opposite sign of β.

The solution is again given by (15), but with a contour C which encloses the cut going from the point $-ik$ to $-i\infty$. As a result we obtain

$$\nu(p) = \frac{\pi}{2V}\left[\left(\frac{2}{\pi}V - \frac{4}{\beta}\right)\delta(p-k) + \frac{4p^2}{\beta^2}\exp\frac{2}{3\beta}(k^3 - p^3)\right], \quad p > k; \quad \nu(p) = 0, \quad p < k. \quad (20)$$

The term with the δ-function in (20) describes the particles which do not change their energy (there is always an elastic component in any inelastic process).[3] The second passing through the critical point leads to capture and an additional smearing-out of the momenta.

If the impact parameter does not lie in a narrow region near the point of closest approach in the nuclear coordinate, then the two critical points can be considered independently, assuming that the system develops adiabatically in the intermediate region.

Neglecting the quantities $(n/\beta)^2$, we obtain formulas (19) and (17) for the capture probability and for the smearing-out effect, respectively, for $p < k$. Thus the final momentum distribution after one collision has the form

$$\nu(p) = \left(1 - 2\pi\frac{n}{\beta}\right)\delta(p-k) + \frac{2\pi n p^2}{\beta^2}\begin{cases}\exp\left[\frac{2}{3\beta}(p^3 - k^3)\right], & p < k\\ \exp\left[\frac{2}{3\beta}(k^3 - p^3)\right], & p > k.\end{cases} \quad (21)$$

The cross section for the collision of two atoms with formation of an ion is obtained by integrating W over the impact parameter ρ from 0 to R_0. For $\rho > R_0$ the capture probability is negligibly small.[1,4] The parameter β depends on ρ according to the formula

$$\beta = \left(\frac{dk_0}{dR}\right)_{R_0} \frac{v_\infty}{R_0}\sqrt{R_0^2 - \rho^2},$$

where v_∞ is the relative velocity of the atoms before the collision (we neglect the curvature of the trajectories). Then

$$\sigma_{\text{cap}} = \frac{4\pi^2}{3} R_0^2 \frac{nk^3}{v_\infty^2 (k_0')^2}\left[\frac{e^{-z}}{z} + \text{Ei}(z)\right],$$

$$z = \frac{2k^3}{3v_\infty k_0'}, \quad k_0' \equiv \left(\frac{dk_0}{dR}\right)_{R_0} \quad (22)$$

[Ei(z) is the exponential integral].

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1 B. M. Smirnov and O. B. Firsov, JETP 47, 232 (1964), Soviet Phys. JETP 20, 156 (1965).

2 Yu. N. Demkov, JETP 46, 1126 (1964), Soviet

Phys. JETP **19**, 762 (1964).
[3] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963. Secs. 139 and 141 [Engl. Transl. Pergamon Press, London, 1958.]
[4] A. V. Chaplik, JETP **45**, 1518 (1963), Soviet Phys. JETP **18**, 1046 (1964).

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