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NEGATIVE ION DECAY IN THE SHORT-RANGE-POTENTIAL APPROXIMATION

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The cross section for electron detachment in collisions between negative ions A^- and atoms A are considered by the short-range-potential method (Firsov and Smirnov[1]). The adiabatic approximation is employed for quasi-stationary states; the nonzero probability for survival of the A_2^- systems is taken into account, and allowance is made accordingly for the energy dependence of the cross section. The energy distribution of the emitted electrons is calculated in the same approximation. The case of different atoms and ions $(A^- + B)$ can be reduced to the case $(A^- + A)$ by renormalizing the parameters of the problem. The results are illustrated by the process $H^- + H \rightarrow H + H + e$ and are compared with the experiments and with other calculations.

1. In[1,2] there was proposed a very simple and lucid model of detachment of an electron in collisions between a negative ion A^- and an atom B. It is based on the following assumptions.

1) There is a critical internuclear distance $R = R_1$, such that when $R < R_1$ the bound state of the system AB^{-1} is unstable. At the point $R = R_1$, the term $E(R)$ of the system AB^- and the term $E_M(R)$ of the system AB are equal, $E(R_1) = E_M(R_1) = D$, and when $R > R_1$ we have $E(R) < E_M(R)$.

2) If we denote by R_{min} the closest-approach distance, then when $R_{min} > R_1$ the detachment probability is equal to zero, and when $R_{min} < R_1$ it is equal to unity.

3) To determine the term of the system AB^- in the region $R \approx R_1$ we can use the model of two zero-radius potentials (the Firsov-Smirnov model).

From assumptions 1) and 2) there follows a formula for the cross section for the detachment of an electron.

$$\sigma_d = \begin{cases} \pi R_1^2(1 - D/E), & E > D \quad (D = E(R_1) > E(\infty)), \\ 0, & E < D. \end{cases}$$

Assumption 3) makes it possible to determine R_1 in terms of the lengths a and b for the scattering of electrons by the atoms A and B. The formula presented above is in good agreement with experiment in a number of cases $(Br^- + He, I^- + He)$, but for certain pairs, for example $H^- + H$, we have not a growth but a decrease of the cross section with increasing energy in the region $E \gg D$, where the formula for σ_d leads to a constant value. This fact can be attributed to the fact that assumption 2) is not correct, for when $R < R_1$ the system AB^- is in a quasistationary state, the decay probability of which during the collision time differs from unity. If the width of the quasistationary term $\Gamma(R)$ at $R < R_1$ is known, then the probability that the system decays within the collision time is determined[3] by

$$w = 1 - \exp\left(-\int \Gamma(\tau)\,d\tau\right),$$

where the integral is taken over the time interval during which $R < R_1$. This formula is a natural generalization of the adiabatic approximation to include quasistationary states, and is valid if the considered quasistationary term is sufficiently far from the other terms. We shall not investigate here the complicated problem of the limits of applicability of this approximation.

Integrating further with respect to the impact parameters, we can obtain σ_d; on the other hand, if we know the real part of the term $\operatorname{Re} E(R) = E_0(R)$ at $R < R_1$, then we can determine the spectrum of the emitted electrons. We use here the model of two zero-radius potentials, proposed by Firsov and Smirnov[1]. Of course, this model is cruder than the variational calculation, but its advantages are simplicity and universality.

Comparison with exact calculation for H_2^- shows that this model describes perfectly satisfactorily the system at $R \approx R_1$. Indeed, it follows from the model that R_1 should be equal to the triplet length of scattering by the hydrogen atom, i.e., 5.7 atomic units, whereas the calculation of[4] gives for the point of intersection of the $^3\Sigma_u$ term of the hydrogen molecule H_2 and of the $^2\Sigma_g$ term of the molecular ion H_2^- a value $R_1 \approx 6$ at.un. An advantage of the Firsov-Smirnov model, besides its simplicity, is also the fact that it is well adapted for the description of the interaction of the bound state with the continuous spectrum, particularly the conversion of the stationary state into a quasistationary one. Therefore the use of this model for the description of the detachment of the electron is quite natural.

2. Let us consider two atoms A and B, assuming that an electron is located on the atom having the lower binding energy. The wave function of the electron in the field of two small-radius potentials is written in the form

$$\psi = A\frac{e^{-\gamma r_a}}{r_a} + B\frac{e^{-\gamma r_b}}{r_b}.$$

Here r_a and r_b are the distances between the electron and the corresponding atoms, and $E = -\gamma^2/2$ is the electron energy. Denoting the reciprocal length for scattering by the atoms A and B by α and β, we impose the usual boundary conditions

$$\left.\frac{d\ln(r_a\psi)}{dr}\right|_{r_a\to 0} = -\alpha, \qquad \left.\frac{d\ln(r_b\psi)}{dr}\right|_{r_b\to 0} = -\beta,$$

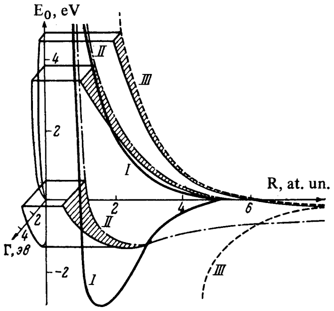

FIG. 1. Terms of molecular ion H_2^-. I–terms of hydrogen molecule, II–terms calculated by Bardsley et al. [14], III–terms calculated by formulas (5) and (6) of the present paper. The width Γ for each term is measured along the third axis.

which lead to the following equation for $W = \gamma R$:

$$(W-a)(W-b)=e^{-2W}, \tag{1}$$

where $a = \alpha R$ and $b = \beta R$. The form of the term $E(R)$ constructed with the aid of the solution of this equation is shown in Fig. 1.

The branch of the term that goes off to $-\infty$ corresponds to positive solutions of the equation. There exist other positive solutions, which are capable of vanishing at $R_1 = (\alpha\beta)^{-1/2}$ and these are paired with negative solutions that come from $-\infty$ on approaching R_1 from the side of large R (not shown in the figure). Such a behavior of the solutions corresponds to the motion of the paired zeroes of the Jost function along the imaginary axis of the complex plane $k = i\gamma$. The zeroes move towards each other with decreasing R, coalesce at a certain value $R = R'$, and then[5] move apart on the plane symmetrically about the imaginary axis. This fact is analogous to the appearance of complex solutions $W = U + iV$ of Eq. (1), which goes over into the system

$$\begin{aligned}(U-a)(U-b)&=e^{-2U}\cos 2V+V^2,\\ V(2U-a-b)&=-e^{-2U}\sin 2V.\end{aligned} \tag{2}$$

The appearance of complex solutions occurs for $\alpha = \beta$ at $R < R' = R_1$, i.e., immediately from the instant of emergence to the continuous spectrum. For $\alpha \neq \beta$ the solutions become complex at $R < R' < R_1$. The interval $R' < R < R_1$ corresponds to the presence of virtual states. The calculation of R' and of the values of W at the instant of appearance of complex solutions will be given below.

3. For the case $\alpha = \beta$ we can obtain from (2) the simple formulas

$$U=1-q-V\operatorname{ctg}V=-\ln\frac{V}{\sin V},$$

$$V^2=e^{-2U}-(U-a)^2,\quad q=1-R/R_1. \tag{3}$$

We seek an approximate solution of the system in the form

$$V^2=cq,\quad U=-q(1-c/3) \tag{4}$$

(c is the coefficient that does not depend on R).

As seen from Fig. 1, the most appreciable contribution to the change of the decay cross section should be made by the region $q \ll 1$ $(0 \leq q \leq 1$, see (3)), i.e., flights at distances close to R_1. In this section, the width is small and the bound states of the molecular ion can exist for quite a long time. We shall therefore regard q as a small parameter and, at the same time, assume constant boundary conditions, namely the value of α, which generally speaking can vary in time. Substituting (4) in the system (2), we get $c \approx 2$, and to determine the width of the level of the negative ion we obtain the expressions

$$\begin{gathered}E\equiv E_0+i\Gamma,\\ E_0=-\frac{U^2-V^2}{2R^2}\approx\frac{\alpha^2}{(1-q)^2}q,\end{gathered} \tag{5}$$

$$\Gamma=\frac{|UV|}{R^2}\approx\frac{\sqrt{2}}{3}\frac{\alpha^2}{(1-q)^2}q^{3/2} \tag{6}$$

The values of E_0 and Γ obtained by exact solution of (2) practically coincide in Fig. 1 with the curves of the approximate formulas (5) and (6).

The cross section for the decay of the negative ion can be represented in the form

$$\sigma_d(v)=\tfrac{1}{2}[\sigma_g(v)+\sigma_u(v)], \tag{7}$$

where $\sigma_g(v)$ and $\sigma_u(v)$ correspond to the cross section for disintegration as a result of departure of two terms of the molecular ion A_2^- to the continuous spectrum at the points R_1 and R_2. In our approximation, we can take into account the motion of the system only for one term $^2\Sigma_g^+$, but, as can be seen from the plot calculated in[4] for the width (given by us as curve II of Fig. 1), the molecule decays very rapidly from the instant that the term $^2\Sigma_g^+$ goes over into the continuous spectrum, and in practice the contribution to the total cross section can be taken into account by setting σ_u simply equal to a constant:

$$\sigma_u=\pi R_2^2. \tag{8}$$

To prove that in our approximation the term going out into the continuous spectrum corresponds to the term Σ_g of the real problem, we can use the reasoning proposed by Firsov. We assign in the spinless case the same scattering length to each of the atoms, without allowance for the presence of the singlet and triplet scatterings. This corresponds to equally oriented spins of the electrons of both atoms in the molecule, and consequently, to an antisymmetrical molecular orbital σ_u. A third weakly-coupled electron joining a molecule of this type falls already on the orbital σ_g, and the lower state of the molecular ion will be the state Σ_u. But we are interested in the higher term Σ_g, which is the first to go into the continuous spectrum. It intersects first the term $^1\Sigma_g^+$ of the hydrogen molecule, but within the framework of our approximation we shall assume that the decay becomes possible at the instant of intersection of the next term $^3\Sigma_u^+$ of the hydrogen molecule. This, naturally, is chosen to be the origin for the construction of curve III in Fig. 1.

The cross section $\sigma_g(v)$ is determined by the formula

$$\sigma_g(v)=2\pi\int_0^{R_1}\rho w\,d\rho, \tag{9}$$

$$w=1-\exp[-2\beta_0 J(p)],$$

$$2\beta_0 J(p)=2\int_0^t\Gamma(\tau)d\tau\approx\frac{4\sqrt{2}}{3}\frac{\alpha}{v}0{,}8\frac{(1-p)^{3/2}}{p}\operatorname{arctg}\frac{\sqrt{1-p^2}}{p},$$

$$\beta_0=\frac{2\sqrt{2}}{3}\frac{\alpha}{v}, \qquad p=\frac{\rho}{R_1}. \tag{10}$$

Here ρ is the impact parameter, the time τ is reckoned from the instant of emergence to the continuous spectrum, and 2t is the time during which the state is unstable. An approximate formula for J(p) is obtained by comparing the upper and lower bounds of the integral $\int \Gamma d\tau$.

The result of an exact calculation of the cross section for the decay of a negative ion in accordance with (6), with allowance from (8) and (9), is shown in Fig. 3 below (curve III). The approximate value is given by formula

$$\sigma_g(v)=\pi R_1^2\left\{1-e^{-\beta_0}\left[\frac{3}{4}F\left(1,\frac{4}{3}\cdot\beta_0\right)+\frac{1}{4}\right]+\frac{\beta_0}{4}[-\mathrm{Ei}(-\beta)]\right\}; \tag{11}$$

F(x, y; z) is the confluent-hypergeometric function resulting from the integration of the exponential within finite limits. At small collision velocities, expanding (6) and (10) in series, we arrive at the expression

$$\sigma_g(v)\approx\pi R_1^2(1-1{,}21\sqrt{v/\alpha}).$$

In calculating the distribution of the energy of the electrons emitted in the decay, we shall assume that at each instant of time their energy is exactly equal to E_0. We then obtain for the distribution function the formula

$$\frac{dP(E_0,\rho)}{dE_0}=2\Gamma(E_0)\frac{\partial\tau(E_0)}{\partial E_0}(w_1+w_2). \tag{12}$$

Here

$$w_1=\exp\left(-2\int\limits_0^{\tau(E_0)}\Gamma(\tau')d\tau'\right)=\exp[-\beta_0 J(p,q)],$$

$$w_2=\exp\left(-2\int\limits_0^{t-\tau(E_0)}\Gamma(\tau')d\tau'\right)=\exp[-\beta_0(2J(p)-J(p,q))],$$

$$J(p,p)=J(p),\quad J(p,q)\approx 0{,}8\frac{q^{3/2}}{p}\left(\operatorname{arctg}\frac{\sqrt{1-p^2}}{p}-\operatorname{arctg}\frac{\sqrt{(1-q)^2-p^2}}{p}\right).$$

The two terms w_1 and w_2 in the right side result from the fact that the specified energy E_0 is reached twice in the collision (during the approach and during the separation).

Using the formula $(v\tau)^2 = R^2 - \rho^2$, we can easily establish with the aid of (5) and (6) the form of the functions $\Gamma(E_0)$ and $\tau(E_0)$. We introduce in place of E_0 the dimensionless variable $s = 2E_0/\alpha^2$, and then we get for q from (6)

$$q(s)=1-\frac{R(s)}{R_1}=1-\frac{\sqrt{2s+1}-1}{s}.$$

When $R\sqrt{2q} \ll 1$, the quantity q behaves like E_0/α^2.

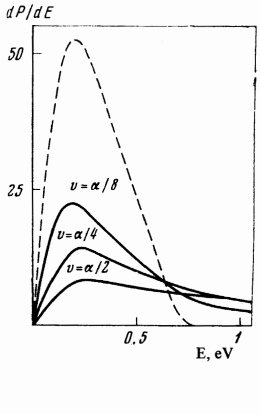

FIG. 2. Distribution of electron energy in the reactions $H^- + H \rightarrow H + H + e$; the dashed line shows the distribution calculated from the data of [2] for a relative collision velocity $v = \alpha/8$.

For the width Γ we obtain the expression

$$\Gamma=\frac{\alpha^2\sqrt{2}}{6}s\sqrt{q}. \tag{13}$$

Expression (2) should be averaged all the impact parameters ρ_- from R_1 to the minimum impact parameter at which the given value of the energy is possible:

$$\frac{dP(E_0)}{dE_0}=\frac{4\sqrt{2}}{3}\frac{1}{\alpha v}q^{3/2}\frac{(1-q)^2}{1+q}\cdot\int\limits_0^{1-q}\frac{q}{\sqrt{(1-q)^2-p^2}}(w_1+w_2)\,dp. \tag{14}$$

If we integrate (14) numerically, we can compare the results of the present investigation (see Fig. 2) with the results obtained earlier in[2]. The picture is qualitatively the same, the positions of the maxima coincide with good accuracy, but at collision velocities $v > 0.4$ at.un. the results are not in as good an agreement.

In[2], the cross section was independent of the velocity, therefore the decay probability was assumed to be equal to unity at $\rho < R_1$. It is seen from this calculation that the cross section decreases noticeably (compared with πR_1^2) even at low velocities. At higher electron energies, the distribution decreases more slowly than in accordance with the data of[2]. This is due to the fact that at small values of R E_0 and Γ tend in this model to infinity, something that should not occur in fact. In addition, the approximation of straight-line flight is not valid for tight collisions.

4. To analyze the $A^- + B$ collisions, we introduce the parameter

$$\delta=\frac{\alpha+\beta}{2\sqrt{\alpha\beta}}-1,$$

which is small compared with unity in all cases of practical interest (α and β are the reciprocal scattering lengths).

We turn first to Eq. (1) with $\alpha \neq \beta$. If we regard the solutions of this equation as the points where the parabola specified by the left side of the equation intersect the exponential curve e^{-2W}, then we can assume that the coalescence of the two zeroes of the Jost function correspond to the point of tangency of the parabola and of the function e^{-2W} (the parabola can be replaced by a straight line and the small quantity W^2 can be discarded). Equating the corresponding coefficients from the equation of the tangent and from the equation $W(a + b) + ab = 0$, we obtain a system for the two unknowns W' and R'. From this we get

$$\frac{1}{R'}=\frac{\sqrt{\alpha\beta}}{2}\left(\frac{1}{1+\delta}+1+\delta\right),$$

$$W'\equiv W(R')=R'\frac{\sqrt{\alpha\beta}}{4}\delta\left(1+\frac{1}{1+\delta}\right).$$

The presence of virtual states makes it necessary to construct the function V in a different form:

$$V^2=lq',\quad U=kq,\quad q'=1-R/R',$$

$$k=\frac{1-3\delta}{3+4\delta},\qquad l=6\frac{1+\delta}{3+4\delta}.$$

However, the quantity R' is always close to R_1 and the presence of virtual states does not change appreciably the course of the solution far from R' and R_1. Therefore, to calculate the cross section of the decay of a negative ion into an atom not of its own kind,

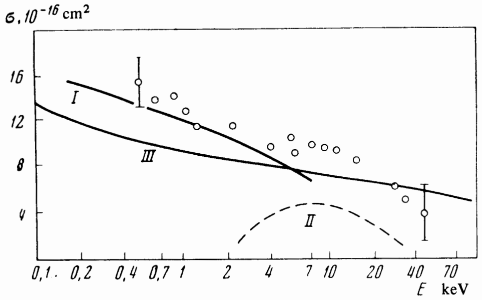

FIG. 3. Cross sections for the decay of a negative hydrogen ion into a hydrogen atom: curve I—calculation of Bardlsey et al. [4], II—calculation of Peach and McDowell in the Born approximation [8], III—our result; points—experiment [7].

formulas (5)—(11) remain valid as before, but the coefficient $\alpha^2\sqrt{2/3}$ is replaced everywhere by $\alpha\beta k\sqrt{l}$. The parameter β_0 in (11) is replaced by

$$\beta_0'(\delta)=\frac{2\sqrt{\alpha\beta}}{V}k\sqrt{l}, \qquad \beta_0'(0)=\beta_0.$$

Substituting the value of Γ obtained in this manner in (13), we can obtain the electron energy distribution.

5. A comparison of the calculation of the decay cross sections with experiment is shown in Fig. 3. Curve I gives the result of Bardsley[6], curve III the results of our calculation, and points are the experimental data of Hummer et al.[7] We assumed for $R_1 = \alpha^{-1}$ the value 6.25, and $R^2 = 3$ (see[4,8]). The calculations of McDowell and Peach[9] in the Born approximation (curve II) do not agree with experiment (dashed curve), while the Bardsley method is not valid for higher energies. Our calculation is likewise not valid at energies larger than 20—25 keV.

As seen from Fig. 1, the values of $E_0(R)$ and $\Gamma(R)$ obtained by us differ quite significantly from the results of Bardsley et al.[4] Of course, this calculation, based on an approximate model, cannot claim high accuracy, in any case when R is much smaller than R_1.

However, the terms obtained in[4], as noted by the authors themselves, are likewise not fully reliable; their course depends strongly on the cutoff parameter. In addition, in calculating the distribution of the electrons it is necessary to know the relative probability of the decay of the hydrogen molecule into singlet and triplet states.

The H_2^- ion is the simplest molecular system in which the bound state goes over into a continuous spectrum in the absence of Rydberg condensation of the levels. Therefore a more accurate calculation of the terms of this system is presently quite urgent.

Besides the $H^- + H$ case, experimental data on detachment cross sections are available for Li^-, Na^-, and K^- collisions with He-Xe[10]. In all these cases, however, the cross section increases with energy, so that the principal role is played here more readily not by the adiabatic but by the dynamic electron-detachment mechanism. The formulas obtained here for the energy distribution are more readily applicable to collisions of ions and atoms of alkali metals. At the present time, such distributions were obtained only for collisions of I^-, Br^-, and Cl^- by He-Kr[10]. In this case, owing to the large energy of electron asymmetry, the small-radius-potential approximation is apparently not applicable.

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