

NEGATIVE ION FORMATION AND DE-EXCITATION OF THE HYDROGEN 2s LEVEL IN SLOW COLLOSIONS

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The $H^* + A \rightleftharpoons H^+ + A^-$ reaction, where H^* is the hydrogen atom in the second quantum level, is considered. The charge exchange probability and probability for radiative de-excitation of the 2s metastable state are found in the adiabatic approximation.

THE binding energy of an electron in negative ions may turn out to be at resonance with the excited levels of certain atoms. In this paper we consider the reaction



where H^* denotes the hydrogen atom in a state with principal number $n = 2$. A similar calculation can be made for strongly excited states of alkali metals. The fact that the energies of the initial and final states are close makes it possible to consider the problem in a two-level approximation, with one of the levels having fourfold degeneracy: $n|l m\rangle = (200), (210), (21 - 1), (21 + 1)$ (we neglect the spin-orbit splitting). If the ionic term E_i lies above the atomic term E_a , then the terms of the quasimolecule corresponding to the initial and final states of the reaction (1) intersect at the point R_0 , which is obtained from the equation $E_i - E_a = 1/R_0$ (we use atomic units).

The reaction (1) was investigated in^[1] for the case of nondegenerate terms. It was shown that the solution of the problem is described by the usual Landau-Zener formula, in which the term splitting parameter is determined by tunnel transitions of the electron. The case considered by us differs in the presence of a larger number of resonant states. As will be shown below, this leads to additional interference effects and to certain numerical differences from the Landau-Zener formula. In addition, the calculation of the probability of transition between components of the degenerate level is of independent interest. The effect observed in this case is the de-excitation of the metastable state 2s of hydrogen in the collisions.

We shall assume the collision to be slow, so that the adiabatic approximation is valid. Let us find the terms of the quasimolecule with the nuclei fixed, with allowance for tunnel transitions of the electron. The wave function of the quasimolecule is sought in the form of a linear combination of four hydrogen functions $\psi_{2s}, \psi_{2p_0}, \psi_{2p_{+1}}, \psi_{2p_{-1}}$ and the wave function φ_i of the negative ion; the latter must be modified with allowance for the Coulomb field of the hydrogen atom nucleus (see^[1,2]). The determination of the terms reduces to a certain generalization of the corresponding calculation for H_2^+ (see^[2]) to include the case of different potential wells and a larger number of resonating states. As a result, when $R \gg 1$ we obtain (the lower index corresponds to the value of the quantum number Λ)

$$E_{-1} = E_{+1} = E_0^{(0)} = E_a, \tag{2}$$

$$E_0^{(2,3)} = 1/2(E_a + E_i - 1/R) \mp 1/2\sqrt{(E_i - E_a - 1/R)^2 + 4\Delta^2},$$

where R is the distance between nuclei,

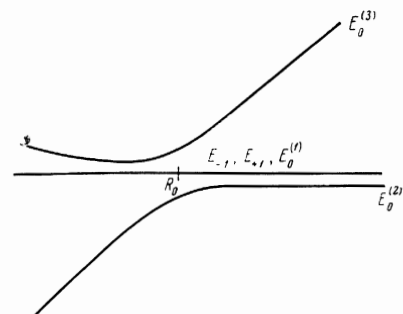
$$\Delta^2 = \langle 2s|i\rangle^2 + \langle 2p_0|i\rangle^2, \quad \langle 2s|i\rangle = \int \left(\psi_{2s} \frac{\partial \varphi_i}{\partial z} - \varphi_i \frac{\partial \psi_{2s}}{\partial z} \right) d\sigma$$

and the expression for $\langle 2p_0|i\rangle$ is similar. The integration is carried out over the z plane, which is perpendicular to the axis of the quasimolecule and bisects this axis. Accurate to numerical factors in the principal order, we have

$$\Delta \sim R \exp[-1/2R(k_0 + 1/2)], \quad k_0 = \sqrt{2|E_i|}, \quad E_a = -1/8.$$

The terms of the quasimolecule with allowance for the splitting are shown in the figure. We shall not write out here the expressions obtained for the adiabatic molecular functions. Their analysis shows that the triply-degenerate term $E_0^{(1)}, E_{+1}, E_{-1}$ corresponds to the functions $2^{-1/2}(\psi_{2s} + \psi_{2p_0}), \psi_{2p_{+1}}$, and $\psi_{2p_{-1}}$. The hydrogen functions have been determined in accordance with^[2]. The terms $E_0^{(2,3)}$ correspond to the combinations $\psi_{2s} - \psi_{2p_0}$ and φ_i . Far from the point of the pseudo-intersection, one of these functions goes over into $2^{-1/2}(\psi_{2s} - \psi_{2p_0})$, and the other into φ_i .

Proceeding to calculate the transition probabilities, let us consider first the variation of the modulus of R . The rotation of the quasimolecule, as will be shown below, leads to corrections that are small in the adiabaticity parameter. Thus, we now consider the interaction of the three states ψ_{2s}, ψ_{2p_0} , and φ_i . It is convenient to solve the problem in the intersecting-terms representation; these terms correspond at large R to



the functions φ_i , $2^{-1/2}(\psi_{2s} + \psi_{2p0})$, and $2^{-1/2}(\psi_{2s} - \psi_{2p0})$.

The system of equations for the probability amplitudes, equivalent to the time-dependent Schrödinger equation, is of the form

$$i\dot{a}_m(t) = \sum_n H_{mn} a_n(t), \quad (3)$$

where H is the total Hamiltonian of the problem, and the quantities a_m are the coefficients of the total wave function, which far from the transition region is equal to

$$\Psi(\mathbf{r}, t) = \frac{a_1(t)}{\sqrt{2}}(\psi_{2s} + \psi_{2p0}) + \frac{a_2(t)}{\sqrt{2}}(\psi_{2s} - \psi_{2p0}) + a_3(t)\varphi_i. \quad (4)$$

The form of the matrix elements H_{mn} can be established by solving the system (3) in the adiabatic approximation and comparing the obtained result with the already known expressions for the adiabatic terms and molecular functions. We then obtain

$$H_{11} = H_{22} = E_a, \quad H_{33} = E_i - 1/R, \quad H_{12} = H_{21} = H_{13} = H_{31} = 0, \quad (5)$$

$$H_{32} = H_{23} = \Delta.$$

Changing over in (3) to new unknown functions

$$b_m = a_m \exp\left\{-i \int \frac{H_{11} + H_{33}}{2} dt\right\}$$

and putting in the transition region

$$\Delta = \Delta(R_0) = \text{const}, \quad E_i - E_a - 1/R = at;$$

we obtain a system of equations for $b_m(t)$:

$$\begin{aligned} i\dot{b}_1 &= \frac{at}{2} b_1, & i\dot{b}_2 &= \frac{at}{2} b_2 + \Delta b_3, \\ i\dot{b}_3 &= -\frac{at}{2} b_3 + \Delta b_2. \end{aligned} \quad (6)$$

Thus, an equation is separated for the state $2^{-1/2}(\psi_{2s} + \psi_{2p0})$. The reason for this is as follows: the matrix elements H_{13} and H_{23} are expressed in terms of the quantities $\langle 2p0|i \rangle$ and $\langle 2s|i \rangle$ introduced above, with H_{13} proportional to $\langle 2p0|i \rangle + \langle 2s|i \rangle$, and H_{23} proportional to $\langle 2p0|i \rangle - \langle 2s|i \rangle$. Since

$$\psi_{2p0} = \frac{1}{\sqrt{8\pi}} \frac{z}{2} e^{-r/2}, \quad \psi_{2s} = \frac{1}{\sqrt{8\pi}} \left(1 - \frac{r}{2}\right) e^{-r/2}$$

and r is close to z in the essential region of integration near the axis of the quasimolecule, we see that $H_{13}/H_{23} \sim R^{-1}$. As to the coupling of the first and second equations in the system (6), this is connected with $\langle 2s|2p0 \rangle$, which is exactly equal to zero for unperturbed hydrogen functions. The next term of the expansion results from the distortion of the hydrogen functions as a result of the presence of the atom A , and its order of smallness is higher than that of R^{-1} . Thus, the results obtained below are valid accurate to R^{-1} .

The solutions of the equations for b_2 and b_3 are expressed in terms of the parabolic-cylinder functions $D_{-i\Delta^2/\alpha}(-e^{i\pi/4}t\sqrt{\alpha})$ and $D_{-i\Delta^2/\alpha-1}(-e^{i\pi/4}t\sqrt{\alpha})$. We present the results for the case when at the start of the collision the hydrogen atom is in the metastable state $2s$. As $t \rightarrow -\infty$, the following initial condition should be satisfied:

$$a_1 = a_2 = e^{-iE_a t} / \sqrt{2}, \quad a_3 = 0. \quad (7)$$

The probabilities of transitions after a single collision, i.e., after two passages through the point of the pseudo-intersection, are expressed by the following formulas:

The formation of the negative ion:

$$\omega_i = 2\varepsilon(1 - \varepsilon) \sin^2(\theta/2), \quad \varepsilon \equiv e^{-2\pi\Delta^2/\alpha}, \quad (8)$$

the probability of going over to the states $2p0$:

$$\begin{aligned} \omega_{2p0} &= 1/2\{(1 - \varepsilon + \varepsilon^2) - \cos\chi(1 - \varepsilon) \\ &\quad - \varepsilon \cos(\theta + \chi) + \varepsilon(1 - \varepsilon) \cos\theta\}; \end{aligned} \quad (9)$$

the probability of remaining in the state $2s$:

$$\begin{aligned} \omega_{2s} &= 1/2\{(1 - \varepsilon + \varepsilon^2) + \cos\chi(1 - \varepsilon) \\ &\quad + \varepsilon \cos(\chi + \theta) + \varepsilon(1 - \varepsilon) \cos\theta\}, \end{aligned} \quad (10)$$

where

$$\begin{aligned} \theta &= \int_0^T (E_0^{(2)} - E_0^{(3)}) - \frac{\pi}{2} + \frac{4\Delta^2}{\alpha} - \frac{4\Delta^2}{\alpha} \ln \frac{\Delta}{\sqrt{\alpha}} + 2 \arg \Gamma\left(1 + i \frac{\Delta^2}{\alpha}\right), \\ \chi &= \int_{-\infty}^{+\infty} (E_0^{(2)} - E_a) dt', \quad T = 2 \int_0^{R_0} \frac{dR}{V_R}, \end{aligned}$$

T is the time between two passages through the pseudo-intersection point, V_R is the radial component of the relative velocity of the nuclei. It is easy to verify that $\omega_i + \omega_{2s} + \omega_{2p0} = 1$. It is seen from formula (8)–(10) that the interference effects, i.e., the oscillations of the probabilities, are connected with the two phases θ and χ . The quantity θ is the usual adiabatic phase shift between two passages through the critical point. Its order of magnitude is determined in the main by the integral in the formula for θ , and is equal to $1/v \gg 1$, with the exception of the narrow region of impact parameters ρ close to R_0 , which makes a small contribution to the total cross section. Thus, formula (8) differs from the usual Landau-Zener formula only in the coefficient 2 in place of 4. This is connected with the fact that at the start of the collision the system is distributed over two molecular states, of which only one contributes to the charge exchange.

The occurrence of the phase shift χ is essentially connected with the presence of the third term. Its magnitude depends on the value of the parameter Δ^2/α and is not necessarily large. Consequently, a situation can arise wherein it is possible to average over θ , but it is impossible to average over χ . This is precisely the phase shift which causes the aforementioned additional interference effects. The corresponding oscillations of the probability occur even after a single passage through the critical point. It is possible to verify that the quantity ω_{2p0} , which determines the probability of de-excitation of the state $2s$, tends to $1/2$ in both limiting cases when $\Delta^2/\alpha \gg 1$ and $\Delta^2/\alpha \ll 1$. The de-excitation cross section as a function of the velocity has a minimum at approximately the same velocity region where the cross section for the formation of the negative ion has a maximum.

It has been assumed in the foregoing calculations that Δ changes little in the region of the transition. The corresponding condition, as can be readily verified, is of the form $\sqrt{v}R_0 \ll 1$.

Let us estimate now the role of the rotation. In the system of equations for the amplitudes, it is necessary

to compare with each other the terms proportional to the tangential v_T and radial components of the relative velocity in the transition region, i.e., v_T/R_0 with $\Delta(R_0)$ and αt . The dimension of the transition region is $t \sim 1/\sqrt{\alpha}$. An estimate shows that the correction that must be introduced into the probability of de-excitation of the state $2s$ as a result of the rotation has a relative order of magnitude \sqrt{v} in the essential region of the impact parameters, i.e., $\rho \lesssim R_0$. The relative order of magnitude of the correction to the charge exchange is v . Thus, the contribution of the rotation of the quasimolecule can be neglected relative to the adiabaticity parameter.

Apparently, it would be of interest to measure independently the quantities ω_1 and ω_{2p_0} in experiments on collisions between long-lived hydrogen in the state $2s$ with some atom forming a negative ion.

For example, for the silver atom $E_1 \approx 2$ eV and R_0

≈ 20 ; the parameter $2\pi\Delta^2/\alpha$ in the essential region of the impact parameters is equal approximately to $10^{-4}/v$. The charge-exchange cross section has a maximum (the de-excitation cross section has a minimum) at $v \sim 10^{-4}$ cm/sec. It is easy to see that in this case all the conditions for the applicability of the results are satisfied, namely $R_0 \gg 1$ and $\sqrt{v}R_0 \ll 1$.

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