

INTERACTION BETWEEN NEGATIVE IONS AND ATOMS

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The properties of a system produced when an atom comes close to a negative ion are investigated. It is assumed that the interaction between the electron and atom is significant in a restricted region of the order of atomic dimensions, and that the weakly bound electron does not affect the properties of the atoms. The dependence of the electron binding energy on the distance between the nuclei is found for such a model in the case when the distances are much greater than the atomic dimensions. On this basis a relation is derived between the electron binding energy and the cross sections for resonance charge exchange for negative ion decay in atomic collisions. A system consisting of spin-1/2 atoms and an electron is considered. It is shown that in the general case the splitting of the energy level of an electron in the field of two widely separated identical spin-1/2 atoms (ions) is half as large as in the case when the atoms are spinless. This result is important in calculating the resonance charge exchange cross section in slow collisions. The possibility of determining the binding energy of negative ions on the basis of the experimental values of the decay and charge exchange cross sections is studied for collisions between the negative ions and atoms.

1. We investigate in the present paper the properties of a quasimolecule made up of an atom and a negative ion. Since the binding energy of the electron in a negative ion is usually much smaller than the ionization energy of the atom, the dimensions of the negative ion exceed the dimensions of the corresponding atom. We assume that the potential of interaction between the electron and the atom is appreciable in a limited region coinciding with the dimensions of the atom, and that the weakly bound electron does not affect the properties of the atom. In this case the action of the atoms on the electron in the quasimolecule in question can be replaced by a boundary condition imposed on the electron wave function at the point where the atom is located. The binding energy of the electron in the quasimolecule is expressed as a function of the distance between the nuclei in terms of these boundary conditions, which are determined by the binding energy of the electron in the negative ion or by the length for the scattering of the slow electron by the atom. It turns out that under certain conditions, the energy level of the quasimolecule crosses the boundary of the continuous spectrum as the atom approaches the negative ion. This makes it possible to express the cross section for the decay of a negative ion colliding with an atom in terms of the length for the scattering of the slow electron from the corresponding atoms.

On the basis of the model proposed, a connec-

tion is established between the cross section for resonant charge exchange of the negative ion on the atom, the relative collision velocity, and the electron binding energy in the negative ion. We shall show that an account of the spin dependence of the boundary condition greatly influences the cross section for the resonant charge exchange and for the decay of the negative ion when the latter collides with the atom.

2. Let us clarify the properties of a quasimolecule made up of a negative ion and an atom separated by large distances R (compared with the atomic dimensions). For the model under consideration and for spinless atoms, the wave function of the electron is described in the region outside the atoms by the Schrödinger equation $-\nabla^2\psi/2 = \epsilon\psi$ (ϵ —electron energy; we use a system of atomic units in which $\hbar = m_{e1} = e^2 = 1$). This equation is satisfied by the wave function

$$\psi = A \frac{e^{-\alpha r_a}}{r_a} + B \frac{e^{-\alpha r_b}}{r_b}. \quad (1)$$

($\alpha = \sqrt{-2\epsilon}$, $r_{a,b}$ —distance from the electron to the nucleus of the corresponding atom), which describes the s-state of the negative ion as $R \rightarrow \infty$. One could solve the Schrödinger equation for the electron inside the atoms and join the obtained solutions on the surface of the atom. However, in view of the smallness of the atomic dimension compared with the dimensions of the negative ion, the action of the internal atomic fields can be

taken into account by imposing a boundary condition on the ψ -function of the electron (1) on the surface of the atom [1]. We then neglect in this model the action of the electron on the atomic fields, i.e., we assume that the boundary conditions on the surfaces of the atoms remain the same when the distances between their nuclei change. If the distances R between nuclei are much larger than the atomic dimensions we obtain

$$\begin{aligned} d \ln(r_a \psi) / dr \Big|_{r_a=r_a^0} &= -k_a = -\alpha + Bf/A, \\ d \ln(r_b \psi) / dr \Big|_{r_b=r_b^0} &= -k_b = -\alpha + Af/B, \end{aligned}$$

where $f = e^{-\alpha R}/R$ and $r_{a,b}^0$ —radius of the corresponding atom.

From the condition for the solvability of a system of the linear homogeneous equations for the coefficients A and B , we obtain the following equation for α :

$$(\alpha - k_1)(\alpha - k_2) - f^2 = 0. \quad (2)$$

It follows from the form of the wave function (1) that a solution of this equation is meaningful when $\alpha > 0$. The case $k_a > 0$ ($k_b > 0$) corresponds at small values of k_a (k_b) to the possibility of formation of a negative ion as $R \rightarrow \infty$ from the given atom with a binding energy $k_a^2/2$ ($k_b^2/2$). If $k_a < 0$ (or $k_b < 0$) or if it assumes a large positive value (~ 1), no negative ion is produced from the given atom. Equation (2) is valid if the model assumption $\alpha r_0 \ll 1$ is satisfied (r_0 —radius of the atom).

An analysis of the solutions of (2) shows that when k_a and k_b have the same sign, $\alpha = 0$ when $R_1 = (k_a k_b)^{-1/2}$ for one of the terms. This means that with further decrease in the distance between the nuclei, the corresponding state goes over into a continuous spectrum ($1 \gg k_a > 0$) or, conversely, the bound state exists only at small distances between the nuclei. On this basis we find that negative ions of inert gases can exist when the distances between nuclei are smaller than 1.3 for He_2^- , 1.6 for Ar_2^- , 3.2 for Kr_2^- , and 5.6 for Xe_2^- (the scattering lengths k^{-1} are taken from [2,3]). However, these distances are not within the range of applicability of the method ($R_1 > 2r_0$). We note that repulsion forces lead to positive scattering lengths, and these scattering lengths are smaller than the effective radius of the atomic forces. The last conclusions are therefore meaningless in the case of repulsion forces ($R_1 < 2r_0$).

3. Assume that an electron can form a bound state with each of the atoms and that at large

distances between the nuclei the electron is near the atom with the smaller binding energy. Then decay of the negative ion takes place at collision impact parameters smaller than $(k_a k_b)^{-1/2}$ and at not too large velocities. Detachment of the electron is possible also in collisions with impact parameters larger than $(k_a k_b)^{-1/2}$, with the ionization having adiabatically low probability for sufficiently large impact parameters.

Using the results of Chaplik [4], let us estimate the impact parameters at which the probability of transition becomes exponentially small. These impact parameters are given by the relation $\text{Re } \Sigma \lesssim -1$, where

$$\Sigma = \frac{i}{2} \int_{t_0}^{t_1} \alpha^2(t) dt,$$

t_0 —complex zero of $\alpha(t)$. Recognizing that the zero of α is located near $t = 0$, which corresponds to collision impact parameters close to $(k_a k_b)^{-1/2}$, we obtain ($x = \rho / (k_a k_b)^{1/2}$)

$$-\Sigma = \frac{4(k_a k_b)^{3/2} (x^2 - 1)^{5/2}}{3v(\sqrt{k_a} - \sqrt{k_b})^4}.$$

If the binding energies of the two negative ions differ from each other by not too much, $-\Sigma$ is a numerically larger quantity (for example, when $\epsilon_a = 4\epsilon_b$ we have $-\Sigma = 133 \text{ kv}^{-1} (x^2 - 1)^{5/2}$; if $k_a = k_b$ we have $-\Sigma = \infty$ at the point of transition into the continuous spectrum). Therefore, with good accuracy, the cross section for the decay of the negative ion is

$$\sigma_{\text{dec}} = \pi / k_a k_b. \quad (3)$$

If $k_a = k_b$, the release of the electron occurs only when $\rho \leq k^{-1}$ and only the odd state decays, so that the cross section for the detachment of the electron is

$$\sigma_{\text{dec}} = \pi / 4\epsilon_{\text{bind}}, \quad (4)$$

ϵ_{bind} —binding energy of the electron in the negative ion.

4. Relation (2) can be used to find the resonance charge exchange cross section when a negative ion collides with an atom of its own kind. The resonance charge exchange cross section is determined from the relation [5,6]

$$\int_0^\infty (\epsilon_u - \epsilon_g) dt \Big|_{\rho=R_1} = \frac{11}{40}, \quad \sigma = \frac{\pi}{2} R_0^2, \quad (5)$$

where $\epsilon_u - \epsilon_g$ —splitting of the electron energy level on approach of the atom.

If the resonance charge exchange cross section is sufficiently large, we can use the asymptotic

form of $\epsilon_u - \epsilon_g$ from (2):

$$\epsilon_u - \epsilon_g = 2ke^{-kR}/R, \quad kR \gg 1. \quad (6)$$

Substituting (6) in (5) and recognizing that no resonance charge exchange takes place for impact parameters smaller than k^{-1} , owing to the decay of the odd state, we obtain

$$\sigma_{\text{res}} = \pi R_0^2/2 - \pi/4k^2, \quad (7a)$$

where R_0 is defined by the condition

$$K_0(kR_0) = 11\nu/80k, \quad kR_0 \gg 1. \quad (7b)$$

Here $K_0(x)$ —Macdonald function, ν —relative collision velocity; inasmuch as the cross sections are large ($kR_0 \gg 1$), we use in (7b) the asymptotic form of $K_0(x)$:

$$K_0(x) \approx (\pi/2x)^{1/2}e^{-x}.$$

5. Usually the electron forms a bound state with an atom having a half-integer spin. It is therefore of practical interest to extend the results to the case when the atoms forming the negative ion of the molecule have spin 1/2. In this case the boundary condition depends essentially on the states of the electron and atom spins, and the effective Hamiltonian of the electron assumes the form

$$H = -1/2\Delta + U_a(\mathbf{r}, R) + U_b(\mathbf{r}, R) + V_a(\mathbf{r}, R)\sigma_a\sigma + V_b(\mathbf{r}, R)\sigma_b\sigma, \quad (8)$$

where σ —electron spin operator; σ_a, σ_b —atom spin operator; the potentials $U_a, U_b, V_a,$ and V_b differ from zero in a limited region of the order of the dimension of the atom near the corresponding atom.

The eigenfunction of the Hamiltonian (8) cannot be expressed in the form of a product of the coordinate function of the electron by the spin function of the electron and the atoms. We therefore seek it in the form

$$\Psi = \Phi_1(\mathbf{r})S_a + \Phi_2(\mathbf{r})T_a^- + \Phi_3(\mathbf{r})T_a^+ \equiv \Psi_1(\mathbf{r})S_b + \Psi_2(\mathbf{r})T_b^- + \Psi_3(\mathbf{r})T_b^+, \quad (9)$$

where we introduce the following notation for the spin functions:

$$S_a = \eta_-(b)2^{-1/2}[\eta_+(a)\eta_- - \eta_-(a)\eta_+], \\ T_a^- = \eta_-(b)2^{-1/2}[\eta_+(a)\eta_- + \eta_-(a)\eta_+], \\ T_a^+ = \eta_+(b)\eta_-(a)\eta_-$$

with similar notation for $S_b, T_b^-,$ and T_b^+ . Here $\eta_{\pm}(a), \eta_{\pm}(b)$ —spin functions of the atom with corresponding sign of the spin projection on the selected direction; η_{\pm} —spin function of the elec-

tron; $\Phi_{1,2,3}$ and $\Psi_{1,2,3}$ —coordinate functions of the electron.

Using the relation between the spin functions, we can easily establish a connection between the coordinate functions $\Phi_{1,2,3}$ and $\Psi_{1,2,3}$:

$$\Psi_1 = 1/2\Phi_1 - 1/2\Phi_2 + \Phi_3/\sqrt{2}, \\ \Psi_2 = -1/2\Phi_1 + 1/2\Phi_2 + \Phi_3/\sqrt{2}, \\ \Psi_3 = \Phi_1/\sqrt{2} + \Phi_2/\sqrt{2}. \quad (10)$$

In the region between the atoms, the coordinate functions satisfying the equation $\nabla^2\psi = \alpha^2\psi$ are sought in the form

$$\Phi_{1,2,3} = A_{1,2,3}\exp(-ar_a)/r_a + B_{1,2,3}\exp(-ar_b)/r_b, \\ \Psi_{1,2,3} = C_{1,2,3}e(-ar_b)/r_b + D_{1,2,3}e(-ar_a)/r_a. \quad (11)$$

The connection between the coefficients A and D or B and C is determined by the relations (10).

Near the atom a, the Hamiltonian of the electron assumes the form $H = -\nabla^2/2 + U_a + V_a\sigma_a\sigma$, so that in this region each term of the first combination of (9) can be an eigenfunction of the Hamiltonian. Therefore the boundary condition on the surface of the atom a necessitates the continuity of the functions Φ_1, Φ_2, Φ_3 and their derivatives. It yields

$$\alpha_a A_1 - fB_1 = 0, \quad \alpha_a' A_2 - fB_2 = 0, \\ \alpha_a' A_3 - fB_3 = 0. \quad (12a)$$

Stipulating continuity of the logarithmic derivative of the functions $\Psi_1, \Psi_2,$ and Ψ_3 on the surface of the atom b, we obtain

$$\alpha_b C_1 - fD_1 = 0, \quad \alpha_b' C_2 - fD_2 = 0, \\ \alpha_b' C_3 - fD_3 = 0. \quad (12b)$$

We have introduced here the notation $\alpha_{a,b} = \alpha - k_{a,b}$; $\alpha'_{a,b} = \alpha - k'_{a,b}$; k_a, k'_a, k_b, k'_b —logarithmic derivatives of the coordinate function of the electron on the surface of the corresponding atom for the singlet and triplet states.

Using the relations between the coefficients A and D or B and C on the basis of (10) and (11), we obtain from the condition of the vanishing of the determinant of the system of linear homogeneous equations

$$(\alpha'_a \alpha'_b - f^2) [f^4 - 1/4 f^2 (\alpha_a \alpha_b + 3\alpha_a \alpha'_b + 3\alpha'_a \alpha_b + \alpha'_a \alpha'_b) + \alpha_a \alpha_b \alpha'_a \alpha'_b] = 0. \quad (13)$$

The possibility of representing (13) in the form of a product of two factors is connected with the fact that the square of the total spin commutes with the Hamiltonian (9). The wave function (10) can therefore be represented by a combination of

two functions that are orthogonal in the spin coordinate, each an eigenfunction of the Hamiltonian. We shall investigate in what follows an equation corresponding to the vanishing of the second factor of (13) and describing the negative ions at large distances between nuclei:

$$f^4 - 1/4 f^2 (\alpha_a \alpha_b + 3\alpha_a \alpha'_b + 3\alpha'_a \alpha_b + \alpha'_a \alpha'_b) + \alpha_a \alpha_b \alpha'_a \alpha'_b = 0. \quad (14)$$

6. Let us consider several interesting particular cases of (14).

1) $k_a = k'_a$, $k_b = k'_b$. In this case the boundary conditions do not depend on the spin. Equation (14) reduces to $(f^2 - \alpha_a \alpha_b)^2 = 0$ and coincides with Eq. (2).

2) $k_b = k'_b$. This is a case in which the spin of one atom is 1/2 and that of the other is zero. Equation (14) becomes $(f^2 - \alpha_a \alpha_b)(f^2 - \alpha'_a \alpha_b) = 0$, i.e., it breaks up into two independent equations, one corresponding to the singlet state of the electron in the atom and the other to the triplet state. The results obtained earlier for the decay and resonance charge exchange cross sections pertain to these two cases.

3) Large distances between nuclei, when we can solve (14) by perturbation theory. The solutions corresponding at $R \rightarrow \infty$ to the bound state take the form

$$\alpha_a = -\frac{(k_a - k'_a)(k_a - k_b)}{2(k_b - k'_a)} + \left\{ \frac{(k_a - k'_a)(k_a - k_b)^2}{4(k_b - k'_a)^2} + \frac{(k_a - k'_a)}{(k_b - k'_a)} \left[\frac{3(k_a - k_b)}{4(k_a - k'_a)} + \frac{1}{4} \right] f^2 \right\}^{1/2};$$

$$\alpha_b = -\frac{(k_b - k'_b)(k_a - k_b)}{2(k_a - k'_b)} - \left\{ \frac{(k_b - k'_b)^2(k_a - k_b)^2}{4(k_b - k'_a)^2} + \frac{(k_b - k'_b)}{(k_a - k'_b)} \left[\frac{3(k_b - k_a)}{4(k_b - k'_a)} + \frac{1}{4} \right] f^2 \right\}^{1/2}.$$

If $k_a = k_b$, $\alpha_{a,b} = \pm f/2$ independently of the states of k'_a and k'_b ($f \ll (k_a - k'_a)/2$, $f \ll (k_b - k'_b)/2$).

4. $k_a = k_b$, $k'_a = k'_b$ —there are two identical atoms with spin 1/2. Equation (14) becomes

$$[f^2 - \alpha_a \alpha'_a + 1/2 f (\alpha_a - \alpha'_a)] \times [f^2 - \alpha_a \alpha'_a - 1/2 f (\alpha_a - \alpha'_a)] = 0.$$

At large distances between the nuclei $f \ll k_a$, k'_a , $|k_a - k'_a|/2$, we have $\alpha = k \pm f/2$ (the roots corresponding to negative α are discarded as $R \rightarrow \infty$), so that as the atoms come together the term-splitting energy is

$$\varepsilon_u - \varepsilon_g = ke^{-hR}/R. \quad (15)$$

The resonance charge exchange cross section is determined from (5):

$$\sigma_{\text{res}} = \pi R_0^2 / 2 - \sigma_{\text{dec}}, \quad K_0(kR_0) = 11\nu / 40k, \quad kR_0 \gg 1. \quad (16)$$

Thus, in the case of atoms with spin 1/2 the asymptotic difference between the terms of the even and odd states (15) turns out to be half as large as in the case of spinless atoms (6). This takes place in the general case. The difference between the terms of the even and odd states is determined in the general case by the relation^[5]

$$\varepsilon_u - \varepsilon_g = \oint_s [\Psi_u \nabla \Psi_g - \Psi_g \nabla \Psi_u] ds, \quad (17)$$

where s —symmetry plane in the coordinate space of the electron; Ψ_u and Ψ_g —even and odd functions of the electron. (The symmetry is now connected with the reflection of the electron relative to the symmetry plane and the permutation of the atomic positions). At large distances between nuclei we have

$$\Psi_{u,g} = 2^{-1/2} [\Psi(\mathbf{r}_a) \mp \Psi(\mathbf{r}_b)],$$

where $\Psi(\mathbf{r}_{a,b}) = \Psi(\mathbf{r}_{a,b}) S_{a,b}$ corresponds to an electron position near the corresponding atom in the singlet state. $\Psi_{u,g}$ can be written in the form

$$\Psi_u = 1/2 \varphi_g(\mathbf{r})(S_a - S_b) + 1/2 \varphi_u(\mathbf{r})(S_a + S_b);$$

$$\Psi_g = 1/2 \varphi_g(\mathbf{r})(S_a + S_b) + 1/2 \varphi_u(\mathbf{r})(S_a - S_b),$$

where the coordinate functions are $\varphi_{u,g} = 2^{-1/2} \times [\varphi(\mathbf{r}_1) \mp \varphi(\mathbf{r}_2)]$. Elimination of the spin coordinates in (17) yields for the electron in the field of the atoms (ions) with spin 1/2:

$$\varepsilon_u - \varepsilon_g = \frac{1}{2} \oint_s [\varphi_u \nabla \varphi_g - \varphi_g \nabla \varphi_u] ds,$$

i.e., a value half as small as for the electrons in the field of spinless atoms (ions) (17).

7. Let us ascertain the possibility that one of the terms will cross the boundary of the continuous spectrum. The crossing point R_1 is given by the relation ($\alpha = 0$)

$$R_1^{-2} = 1/8(k_a k_b + 3k'_a k_b + 3k_a k'_b + k'_a k'_b) \pm 1/8[(k_a k_b + 3k_a k'_b + 3k'_a k_b + k'_a k'_b)^2 - 64k_a k_b k'_a k'_b]^{1/2}. \quad (18)$$

Equation (18) for R_1 has a real positive solution if the relation between the parameters k_a , k'_a , k_b , and k'_b is such that the radicand is positive. This condition is always satisfied if k_a , k'_a , k_b , and k'_b are of the same sign. Two positive solutions then exist for (18) and if $1 \gg k_a$ and $b > 0$ then

a minus sign in (18) signifies that the state bound at $R \rightarrow \infty$ goes over to the continuous spectrum.

If any one among the parameters k_a , k'_a , k_b , or k'_b is opposite in sign to all the others then (18) always has one positive solution. If $1 \gg k_{a,b} > 0$ while k'_a and k'_b are negative, then the probability of (18) having a real solution is low. For example, for the existence of a real solution of (18) in the resonant case $k_a = k_b$, $k'_a = k'_b < 0$ it is necessary to satisfy the conditions $ka \leq |k'_a|/14$ or $|k'_a| \leq k_a/14$. The former corresponds to excessively short lengths for the elastic scattering of the electron by the atom and is of little likelihood, while the latter corresponds to excessively low energies of the electron virtual level (very large scattering lengths), and is therefore not realizable in practice.

In all cases when a positive real solution of (18) exists, the cross section for detachment of an electron in a collision between a negative ion and the atom (as in Sec. 3) is determined by the relation $\sigma = \pi R_1^2 \sim k^{-2}$.

8. Let us ascertain the possibility of applying the obtained results to real collisions of negative ions with atoms. The limited nature of the employed model is due on the one hand, to the neglect of the long-range polarization forces compared with the binding energy and, on the other, to the neglect of the influence of the weakly bound electron on the atomic core. The results obtained therefore describe only in general outlines the ionization following collision between a negative ion with atoms. (The weak dependence of the ionization cross section on the collision velocity, obtained when the present model is used, is in good agreement with experiment^[7]). The results obtained for resonant charge exchange of a negative ion by an atom of its own kind are exact (under the condition $kR_0 \gg 1$, $kr_0 \ll 1$), since they are connected with the use of perturbation theory.

9. One of the authors^[5] has pointed out the possibility of determining the binding energies of negative ions from the slope of the $[2\sigma_{\text{RES}}(v)/\pi]^{1/2}$ curve. This is convenient in investigations of negative ions with low ionization energy, for in this case there are no other reliable experimental methods for determining the binding energy. Relations (7) and (16) provide a connection between the cross section for resonance charge exchange of negative ions and their binding energy. These relations are asymptotically exact if $kR_0 \gg 1$, and $kr_0 \ll 1$, and are more convenient for determining the binding energies of negative ions.

A third method of determining the binding energy of negative ions with the aid of the cross sections of collision processes is based on the

connection between the decay cross section and the affinity energy of the electron in the negative ion (3). It is most convenient in the experiment to scatter the investigated ion from atoms of an inert gas, where the electron scattering length k^{-1} is positive (argon, krypton, xenon). The lengths for scattering the electron by inert-gas atoms are reliably determined from the shift of the spectral lines of excited alkali atoms present in the given inert gas^[2].

10. The accuracy of the model can be checked with the negative hydrogen ion as an example, for in this case one can calculate with sufficient accuracy both the electron binding energy^[8] and the length for the scattering of the electron by the hydrogen atom in the singlet and triplet states^[9]. The boundary condition imposed on the electron in the negative hydrogen ion is $k = (2\epsilon_{\text{bind}})^{1/2} = 0.265$; the boundary conditions corresponding to the scattering of an electron with zero energy in the singlet state by a hydrogen atom is $k = 0.175$. On the other hand, the model considered in the present paper presupposes that the boundary conditions imposed on its wave functions remain unchanged when the electron energy changes.

The cross section for the decay of a negative hydrogen ion colliding with a hydrogen atom, calculated from the lengths for the scattering of a zero-energy electron by a hydrogen atom^[9], $1/k = 5.7$ and $1/k' = 1.7$, amounts to $8 \times 10^{-16} \text{ cm}^2$. This agrees with the experimental cross section for the disintegration of a negative hydrogen ion colliding with a hydrogen atom^[10], $\sim 10^{-15} \text{ cm}^2$.

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