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 connection 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

$$-\frac{\hbar^2}{2m_e} \phi(R, \alpha) = \varepsilon \phi(R, \alpha)$$

($\varepsilon$—electron energy; we use a system of atomic units in which $\hbar = m_e = e^2 = 1$). This equation is satisfied by the wave function

$$\phi(R, \alpha) = A \frac{e^{-r_a}}{r_a} + B \frac{e^{-r_b}}{r_b}.$$  \hspace{1cm} (1)

($\alpha = \sqrt{-2\varepsilon}$, $r_{a,b}$—distance from the electron to the nucleus of the corresponding atom), which describes the $s$-state of the negative ion as $R \to \infty$. 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
When $k_a$ and $k_b$ have the same sign, the forces (reflecting a Born-Oppenheimer approximation) act on the core nuclei only, since with further decrease in the distances between the nuclei, the corresponding state goes over into a continuous spectrum. The last conclusions are therefore meaningless in the case of repulsion forces. The last conclusions are therefore meaningless in the case of repulsion forces (as, for example, when the distances $R$ between nuclei are smaller than the effective radius of the corresponding atom).

An analysis of the solutions of (2) shows that when $k_a$ and $k_b$ have the same sign, $\alpha = 0$ when $R = (k_a k_b)^{-1/2}$ for one of the terms. This means that with further decrease in the distances between the nuclei, the corresponding state goes over into a continuous spectrum (if $k_a < 0$ or $k_b < 0$) or if it assumes a large positive value ($\sim 1$), no negative ion is produced from the given atom. Equation (2) is valid if the model assumption $r_\alpha \ll \alpha$ is satisfied ($r_c$—radius of the corresponding atom).

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

\[
\epsilon_u - \epsilon_g = 2ke^{-kR} / R, \quad kR \gg 1.
\]

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

\[
\sigma_{res} = \pi R_0^2 / 2 - \pi / 4k^2,
\]

where \( R_0 \) is defined by the condition

\[
K_0(kR_0) = 11v / 80k, \quad kR_0 \gg 1.
\]

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

\[
K_0(x) \approx (\pi / 2x)^{1/4} e^{-x}.
\]

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

\[
H = -\frac{1}{2}\Delta + U_a(r, R) + U_b(r, R)
\]

\[
+ V_a(r, R)\sigma_a\sigma + V_b(r, R)\sigma_b\sigma,
\]

where \( \sigma \)—electron spin operator; \( \sigma_a, \sigma_b \)—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 its form in the form

\[
\Psi = \Phi_1(r)S_a + \Phi_2(r)T_a^- + \Phi_3(r)T_a^+
\]

\[
= \Psi_1(r)S_b + \Psi_2(r)T_b^- + \Psi_3(r)T_b^+,
\]

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 \( S_b, T_a^-, \) and \( T_b^+ \). Here \( \eta_+(a), \eta_-(b) \)—spin functions of the atom with corresponding sign of the spin projection on the selected direction; \( \eta_+ \)—spin function of the electron; \( \Phi_1, \Phi_2, \Phi_3 \) and \( \Psi_1, \Psi_2, \Psi_3 \)—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 \( \Psi_{1,2,3} \):

\[
\Psi_1 = \frac{1}{2}\Phi_1 - \frac{1}{2}\Phi_2 + \Phi_3 / \sqrt{2},
\]

\[
\Psi_2 = -\frac{1}{2}\Phi_1 + \frac{1}{2}\Phi_2 + \Phi_3 / \sqrt{2},
\]

\[
\Psi_3 = \Phi_1 / \sqrt{2} + \Phi_2 / \sqrt{2}.
\]

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

\[
\Phi_1, 2, 3 = A_1, 2, 3 \exp (-\alpha r_a) / r_a + B_1, 2, 3 \exp (-\alpha r_b) / r_b,
\]

\[
\Psi_1, 2, 3 = C_1, 2, 3 \exp (-\alpha r_a) / r_a + D_1, 2, 3 \exp (-\alpha r_b) / r_b. \quad (11)
\]

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 \( H = -V^2/2 + U_a + V_a\alpha_2\sigma \), 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 \( \Phi_1, \Phi_2, \Phi_3 \) and their derivatives. It yields

\[
a_oA_1 - fB_1 = 0, \quad a_oA_2 - fB_2 = 0,
\]

\[
a_oA_3 - fB_3 = 0. \quad (12a)
\]

Stipulating continuity of the logarithmic derivative of the functions \( \Psi_1, \Psi_2, \) and \( \Psi_3 \) on the surface of the atom \( b \), we obtain

\[
a_oC_1 - fD_1 = 0, \quad a_oC_2 - fD_2 = \theta,
\]

\[
a_oC_3 - fD_3 = 0. \quad (12b)
\]

We have introduced here the notation \( a_o = \alpha - k_{a,b}; \quad a_o' = \alpha - k_{a,b}^2; \quad a_o^3 = \alpha - k_{a,b}^3 \)—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

\[
(a_o^3a_o^3 - f)[f^4 - \frac{1}{4}F(a_o^3a_o^3 + 3a_o^3a_o^3)] = 0.
\]

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:

\[ f^2 - \frac{1}{2} f^2 (a_0 a' + 3a_0 a' + 3a_0 a + a_0 a') + a_0 a + a_0 a' = 0. \quad (14) \]

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

1) \( k_0 = k_0', k_0 = k_0' \). In this case the boundary conditions do not depend on the spin. Equation (14) reduces to \((f^2 - \alpha_0 a_0)^2 \) and coincides with Eq. (2).

2) \( k_0 = k_0' \). This is a case in which the spin of one atom is 1/2 and that of the other is zero. Equation (14) becomes \((f^2 - \alpha_0 a_0 f)^2 \) and 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 \( R \to \infty \) to the bound state take the form

\[ \alpha = \frac{(k_0 - k_0')(k_0 - k_0)}{2(k_0 - k_0')} + \left( \frac{(k_0 - k_0')(k_0 - k_0)^2}{k_0(k_0 - k_0')} \right)^t \frac{1}{4} f^2 + \left( \frac{3(k_0 - k_0)(k_0 - k_0)^2}{k_0(k_0 - k_0')} + \frac{1}{4} \right) f^2 \]

\[ \alpha_0 = \frac{(k_0 - k_0')(k_0 - k_0)}{2(k_0 - k_0')} - \left( \frac{(k_0 - k_0')(k_0 - k_0)^2}{k_0(k_0 - k_0')} \right)^t \frac{1}{4} f^2 + \left( \frac{3(k_0 - k_0)(k_0 - k_0)^2}{k_0(k_0 - k_0')} + \frac{1}{4} \right) f^2 \]

If \( k_0 = k_0' \), \( a_0, b = 1/2 \) independently of the states of \( k_0' \) and \( k_0' \) (\( f \ll (k_0 - k_0)/2 \), \( f \ll (k_0 - k_0)/2 \)).

4. \( k_0 = k_0', k_0 = k_0' \) are two identical atoms with spin 1/2. Equation (14) becomes

\[ f^2 - a_0 a' + \frac{1}{2} f^2 (a_0 - a') = 0. \]

At large distances between the nuclei \( f \ll k_0, k_0' \), \( k_0', k_0 = k_0'/2 \), we have \( \alpha = k \pm f/2 \) (the roots corresponding to negative \( \alpha \) are discarded as \( R \to \infty \)), so that as the atoms come together the term-splitting energy is

\[ \varepsilon_n = \varepsilon_0 = k e^{-\kappa R} / R. \quad (15) \]

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

\[ \sigma_{res} = \pi k_R^2 / 2 - \sigma_{dec}, \quad k_R(k_R) = 11n / 40k, \quad k_R \gg 1. \quad (16) \]

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

\[ \varepsilon_n - \varepsilon_n = \frac{\pi}{2} \left[ \Psi_u \nabla \Psi_d - \Psi_d \nabla \Psi_u \right] ds, \quad (17) \]

where \( s \)-symmetry plane in the coordinate space of the electron; \( \Psi_u \) and \( \Psi_d \)-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

\[ \Psi_u, d = 2^{-\frac{1}{2}} \left[ \Psi (r_1) \mp \Psi (r_2) \right], \]

where \( \Psi (r_1, 1) \) corresponds to an electron position near the corresponding atom in the singlet state. \( \Psi_u, d \) can be written in the form

\[ \Psi_u = \frac{1}{2} \overline{\varphi_1 (r, (S_a - S_b)) + 1} \overline{\varphi_2 (r, (S_a + S_b))}, \]

\[ \Psi_d = \frac{1}{2} \overline{\varphi_1 (r, (S_a + S_b)) + 1} \overline{\varphi_2 (r, (S_a - S_b))}, \]

where the coordinate functions \( \varphi_i \) are of the same sign. Two positive solutions exist for (18) and if \( 1 \gg k_0 \) 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 \( k_\alpha, k'_\alpha, k_\beta \),
or \( k'_\beta \) is opposite in sign to all the others then
(18) always has one positive solution. If \( 1 \gg k_\alpha, k_\beta > 0 \) while \( k'_\alpha \) and \( k'_\beta \) are negative, then the prob-
ability of (18) having a real solution is low. For ex-
ample, for the existence of a real solution of
(18) in the resonant case \( k_\alpha = k_\beta, k'_\alpha = k'_\beta < 0 \) it
is necessary to satisfy the conditions \( k_\alpha \leq k'_\alpha \)
/14 or \( |k'_\beta| \leq k_\beta /14 \). The former corresponds
to excessively short lengths for the elastic scat-
tering of the electron by the atom and is of little
likelihood, while the latter corresponds to exces-
sively 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 \( \sigma = \pi R_0^2 \sim k^{-2} \n\)
8. Let us ascertain the possibility of applying
the obtained results to real collisions of negative
ions with atoms. The limited nature of the em-
ployed 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 elec-
tron 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 ion-
ization cross section on the collision velocity, ob-
tained when the present model is used, is in good
agreement with experiment [5].) The results ob-
tained 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 \( [2\sigma_{res}'(v)]
/\pi \) \( \sqrt{2} \) curve. This is convenient in investigations of
binding energies of negative ions with low ionization energy, for in
this case there are no other reliable experimental
methods for determining the binding energy. Re-
lations (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 en-
ergy 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 reli-
bly 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 ac-
curacy both the electron binding energy [5] and
for the scattering of the electron by the hydrogen
atom in the singlet and triplet states [5].

The boundary condition imposed on the electron
in the negative hydrogen ion is \( k = (2E_{bind})^{1/2} \)
= 0.265; the boundary conditions corresponding to
the scattering of an electron with zero energy in
a 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 con-
ditions imposed on its wave functions remain un-
changed when the electron energy changes.

The cross section for the decay of a negative
hydrogen ion colliding with a hydrogen atom, cal-
culated from the lengths for the scattering of a
zero-energy electron by a hydrogen atom [5], \( 1/k \)
= 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 [16], \( \sim 10^{-15} \) \( \text{cm}^2 \).

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1. L. D. Landau and E. M. Lifshitz, Quantum
Mechanics, Addison-Wesley, 1958, Sec. 109.
2. H. S. W. Massey and E. H. S. Burhop, Elec-
tronic and Ionic Impact Phenomena, Oxford Univ.
Press, 1952.
3. Martynenko, Firsov, and Chibisov, JETP 44,
4. A. V. Chaplik, JETP 45, 1518 (1963), Soviet
Phys. JETP 18, 1046 (1964).
6. B. M. Smirnov, JETP 46, 1017 (1964), Soviet
7. J. B. Hasted, Atomic and Molecular Processes,
9. A. Temkin and J. S. Lamkin, Phys. Rev. 121,
788, (1960).
10. Hummer, Stebbings, and Fite, Phys. Rev. 119,
668 (1960).

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