

*ELECTRON EXCHANGE AND CHANGES IN THE HYPERFINE STATE OF COLLIDING
ALKALINE METAL ATOMS*

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Submitted to JETP editor October 3, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **48**, 939-945 (March, 1965)

The asymptotically exact value of the exchange interaction between two alkaline metal atoms is calculated for large distances between the nuclei. The exchange interaction is found to exceed the Van der Waals interaction up to large distances between nuclei. The result is used to determine the cross section for electron exchange and the cross section for the variation of the hyperfine state of colliding alkaline metal atoms.

1. The hyperfine state of the atoms of alkaline metals is determined by the mutual orientation of the spins of the nucleus and of the valence electron. When atoms collide, the strongest mechanism for the change in this state is exchange of valence electrons with oppositely directed spins^[1]. The effective cross sections for electron exchange in the case of an adiabatically slow collision of the atoms is determined completely by the magnitude of the electron energy splitting as the atoms come close together, that is, by the difference in the terms of the symmetrical and antisymmetrical states. The cross section for electron exchange turns out to be large compared with the characteristic atomic cross section, so that to determine the latter it is necessary to know the asymptotic value of the difference of the terms at large distances between nuclei.

Dalgarno^[2] and Smith^[3] calculated the cross section for electron exchange in collisions between two hydrogen atoms, using the term-difference value obtained by the Heitler-London method. As shown by Herring^[4] and by Gor'kov and Pitaevskii^[5], the Heitler-London method is fundamentally incorrect in calculations of the asymptotic value of the term difference. Gor'kov and Pitaevskii^[5], and also Herring and Flicker^[6], calculated the asymptotically exact value of the term difference of the symmetrical and antisymmetrical states for two hydrogen atoms separated by large distance. In the present paper we extend their method to include the atoms of alkaline metals. The obtained value of the term difference is then used to calculate the cross section for the exchange of electrons and the probability of variation of the hyperfine state upon collision of these atoms. It is also shown that the exchange interaction of these atoms prevails over the Van der Waals

interaction even at very large distances between nuclei.

2. Let us calculate the probability of electron exchange in collisions between atoms. If the first electron was situated prior to the collision at the atom a and the second at the atom b, then the wave function of the electrons prior to the collision was of the form

$$\Psi = \varphi_a(r_1)\psi_b(r_2), \quad (1)$$

where $r_{1,2}$ —coordinates of the corresponding electron and φ_a and ψ_b —wave functions of the electrons with center in the nucleus of the given atom. At finite distances R between nuclei, the system of eigenfunctions of the Hamiltonian H of the electrons breaks up into symmetrical and antisymmetrical eigenfunctions Ψ_S and Ψ_A , corresponding to zero and unity total electron spin, respectively. Then

$$H\Psi_S = E_S(R)\Psi_S, \quad H\Psi_A = E_A(R)\Psi_A,$$

that is, the wave functions and their eigenvalues depend on the distance between the nuclei as a parameter, and as $R \rightarrow \infty$ we have

$$\Psi_{S,A} = 2^{-1/2}[\varphi_a(r_1)\psi_b(r_2) \pm \varphi_a(r_2)\psi_b(r_1)].$$

Neglecting the transitions to excited states, we seek the wave function of the electrons of the colliding atoms in the form

$$\Psi = c_A\Psi_A + c_S\Psi_S.$$

We substitute this expression into the Schrödinger equation $i\partial\Psi/\partial t = H\Psi$, multiply from the left by Ψ_A and Ψ_S , and integrate over the electron coordinates. Neglecting the inelastic transitions between the symmetrical and antisymmetrical state, we obtain

$$c_{A,S} = c_{A,S}^0 \exp\left[-i \int_{-\infty}^t E_{A,S}(R) dt\right]$$

(we are using a system of atomic units $\hbar = m_e$, $e^2 = 1$). In accordance with (1), $c_A = c_S = 2^{-1/2}$ when $t \rightarrow -\infty$, and therefore $c_A^0 = c_S^0 = 2^{-1/2}$. The probability for electron exchange is therefore

$$W_{\text{exch}} = |\langle \varphi_a(r_2) \psi_b(r_1) | \Psi(t \rightarrow \infty) \rangle|^2 = \sin^2 \left(\int_{-\infty}^{+\infty} \frac{E_A - E_S}{2} dt \right). \quad (2)$$

Thus, the problem of determining the exchange cross section reduces to finding the electron energy splitting as the atoms come together. We see that the probability of exchange is determined in the same manner as the probability for resonance charge exchange^[7].

3. Let us calculate the asymptotic value of $E_A - E_S$ at large distances between the nuclei. Since this quantity is exponentially small as $R \rightarrow \infty$, Ψ_A and Ψ_S are solutions of the same Schrödinger equation, and therefore, with exponential accuracy, they constitute the sum and difference of identical functions

$$\Psi_{S,A} = (\Psi_I \pm \Psi_{II}) / \sqrt{2}.$$

Here Ψ_I and Ψ_{II} satisfy the same Schrödinger equation as Ψ_A and Ψ_S .

The magnitude of the splitting of the electron energy level $E_A - E_S$ for $R \rightarrow \infty$ can be easily obtained from the Schrödinger equation for the functions Ψ_A and Ψ_S ^[5,6]:

$$E_A - E_S = \int_S \left(\Psi_I \frac{\partial \Psi_{II}}{\partial z_1} - \Psi_{II} \frac{\partial \Psi_I}{\partial z_1} \right)_{z_1=z_2} d\tau_2 dx_1 dy_1, \quad (3)$$

where $d\tau_2$, dx_1 , and dy_1 are the volume and surface elements in the coordinate space of the corresponding electron. It is convenient to choose as the surface S the hypersurface $z_1 = z_2$ (the z axes coincide in the electron space with the directions of the axis joining the nuclei).

The wave functions $\Psi_{I,II}$ satisfy the equation $H\Psi = E\Psi$, where

$$H = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + V_a(\mathbf{r}_1 - \mathbf{a}) + V_a(\mathbf{r}_2 - \mathbf{a}) + V_b(\mathbf{r}_1 + \mathbf{a}) + V_b(\mathbf{r}_2 + \mathbf{a}) - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}; \quad (4)$$

the electron energy, accurate to terms $\sim 1/R^2$, is

$$E = -\frac{\alpha^2}{2} - \frac{\beta^2}{2} - \frac{1}{R}. \quad (5)$$

Here $\mathbf{a} = \mathbf{R}/2$, $\alpha^2/2$ and $\beta^2/2$ are the electron binding energies in the given atom, while V_a and V_b are the effective potentials of interaction between the electron and the corresponding atomic residue, which is of the Coulomb type far from

the atoms: $V_{a,b}(r) \rightarrow -1/r$, $r \rightarrow \infty$. In the main region of electron distribution, the wave functions Ψ_I and Ψ_{II} are products of the atomic wave functions (1), with the asymptotic behavior of the radial atomic wave functions of the electron in the Coulomb field of the atomic residue being determined by the formulas

$$\varphi_a(r) = Ar^{1/\alpha-1}e^{-\alpha r}, \quad \psi_b = Br^{1/\beta-1}e^{-\beta r}. \quad (6)$$

The coefficients A and B are determined by the behavior of the wave functions of the electrons inside the atoms.

We see that the potential of the electron-electron interaction and of the interaction with the "foreign" atomic residue in the main part of the region $\alpha(|\mathbf{r} - \mathbf{a}| - R/2) + \beta(|\mathbf{r} + \mathbf{a}| - R/2) \sim 1$, which determines the magnitude of the integral (3), is small compared with the electron energy and changes little as the electron is displaced by a distance on the order of $1/\alpha$ or $1/\beta$. It is therefore convenient to use the quasiclassical approximation to find the functions $\Psi_{I,II}$. We determine the wave functions $\Psi_{I,II}$ in the region near the z axis essential to the integral (3), and assume that a Coulomb interaction takes place there between the electron and the atomic residues. Substituting in the Schrödinger equation

$$\Psi_{I,II} = \chi_{I,II} \Psi_{I,II}^{\text{at}},$$

where the function χ is smooth compared with Ψ^{at} , and neglecting the second derivatives with respect to χ , we obtain for χ a linear differential equation of first order in two variables.

Like Gor'kov and Pitaevskii^[5] or Herring and Flicker^[6], we reduce this equation, by means of a change of variable, to a differential equation in one variable, in which the second variable is contained as a parameter. We solve this equation, taking into account the fact that $\chi_I \rightarrow 1$ as $z_2 \rightarrow a$ if $z_1 + z_2 > 0$, and $\chi_I \rightarrow 1$ as $z_1 \rightarrow -a$ if $z_1 + z_2 < 0$. As a result we obtain the following: When $z_1 + z_2 > 0$

$$\begin{aligned} \chi_I = \exp & \left[-\frac{1}{2\beta} - \frac{\beta\eta - 2\alpha\xi}{2\alpha\beta(\alpha + \beta)} \right] \\ & \times \left\{ [([2(\beta - \alpha)\xi + (\alpha + \beta)\eta]^2 + [(\alpha + \beta)\rho_{12}]^2)^{1/2} \right. \\ & \left. - [2(\beta - \alpha)\xi + (\alpha + \beta)\eta]]^{1/(\alpha + \beta)} \right. \\ & \times \left[\frac{(\alpha + \beta)^2}{\beta} a - \frac{2}{\beta} (\alpha^2 + \beta^2)\xi \right]^{1/\alpha} [2a(\alpha + \beta)]^{1/\beta} \left. \right\} \\ & \times \left\{ \left(\left[\frac{2}{\beta} (\alpha^2 + \beta^2)\xi - a \frac{(\alpha + \beta)^2}{\beta} \right]^2 + [(\alpha + \beta)\rho_{12}]^2 \right)^{1/2} \right. \\ & \left. + \frac{(\alpha + \beta)^2}{\beta} a - \frac{2(\alpha^2 + \beta^2)}{\beta} \xi \right\}^{-1/(\alpha + \beta)} \end{aligned}$$

$$\begin{aligned} & \times [(\alpha + \beta)a - 2\beta\xi - \alpha\eta]^{-1/\alpha} \\ & \times [(\alpha + \beta)a + 2\alpha\xi - \beta\eta]^{-1/\beta}, \end{aligned} \quad (7a)$$

when $z_1 + z_2 < 0$

$$\begin{aligned} \chi_I = & \left\{ [2(\beta - \alpha)\xi + (\alpha + \beta)\eta]^2 + [(\alpha + \beta)\rho_{12}]^2 \right\}^{1/2(\alpha+\beta)} \\ & - [2(\beta - \alpha)\xi + (\alpha + \beta)\eta] \Big\}^{1/(\alpha+\beta)} \\ & \times \exp \left[-\frac{1}{2\alpha} - \frac{2\beta\xi + \alpha\eta}{2\alpha(\alpha + \beta)} \right] \\ & \times [2\alpha(\alpha + \beta)]^{1/\alpha} \left[-\frac{(\alpha + \beta)^2}{\alpha} a + \frac{2}{\alpha} (\alpha^2 + \beta^2)\xi \right]^{1/\beta} \\ & \times \left\{ \left(\left[\frac{2(\alpha^2 + \beta^2)}{\alpha} \xi + \frac{a(\alpha + \beta)^2}{\alpha} \right]^2 + [(\alpha + \beta)\rho_{12}]^2 \right)^{1/2} \right. \\ & \left. + \frac{a(\alpha + \beta)^2}{\alpha} + \frac{2(\alpha^2 + \beta^2)}{\alpha} \xi \right\}^{-1/(\alpha+\beta)} \\ & \times [(\alpha + \beta)a - 2R\xi - \alpha\eta]^{-1/\alpha} [(\alpha + \beta)a + 2\alpha\xi - \beta\eta]^{-1/\beta}, \end{aligned} \quad (7b)$$

where

$$\begin{aligned} \rho_{12} &= [(x_1 - x_2)^2 + (y_1 - y_2)^2]^{1/2}, \\ \xi &= (\alpha + \beta)(\beta z_1 + \alpha z_2) / 2(\alpha^2 + \beta^2), \\ \eta &= (\alpha z_1 - \beta z_2)(\alpha + \beta) / (\alpha^2 + \beta^2); \end{aligned}$$

χ_{II} is obtained from χ_I by replacing z_1 with z_2 .

Substituting the obtained expressions in (3) and differentiating under the integral sign only the exponential in (4), we obtain ultimately

$$E_A - E_S = R^{2/\alpha+2/\beta-1/(\alpha+\beta)-1} e^{-(\alpha+\beta)R} J(\alpha, \beta, R);$$

$$J(\alpha, \beta, R) = A^2 B^2 2^{-2-2/(\alpha+\beta)} \Gamma\left(\frac{1}{\alpha + \beta}\right) \left(\frac{2}{\alpha + \beta}\right)^{2+1/(\alpha+\beta)}$$

$$\begin{aligned} & \times \left\{ \left(\frac{\alpha + \beta}{2\beta} \right)^{2/\alpha-2/(\alpha+\beta)} \int_0^1 e^{(y-1)/\beta+R(\beta-\alpha)y} (1-y)^{2/\beta-1/(\alpha+\beta)} \right. \\ & \times (1+y)^{2/\alpha-2/\beta+1/(\alpha+\beta)} \left[1 + \frac{\beta - \alpha}{\beta + \alpha} y \right]^{-2-1/(\alpha+\beta)} dy \\ & \left. + \left(\frac{\alpha + \beta}{2\alpha} \right)^{2/\beta-2/(\alpha+\beta)} \int_0^1 \exp \left[\frac{y-1}{\alpha} + R(\alpha - \beta)y \right] \right. \\ & \times (1-y)^{2/\alpha-1/(\alpha+\beta)} (1+y)^{2/\beta-2/\alpha+1/(\alpha+\beta)} \\ & \left. \times \left[1 + \frac{\alpha - \beta}{\alpha + \beta} y \right]^{-2-1/(\alpha+\beta)} dy \right\}. \end{aligned} \quad (8)$$

This relation is valid if for $r \sim R/2$ the atomic wave functions coincide with their asymptotic value, and their change with increasing r is connected essentially with the attenuation of the exponential:

$$R\alpha^2 / 2 \gg 1, \quad R\beta^2 / 2 \gg 1. \quad (9)$$

If $\alpha = \beta$, the integral J does not depend on R :

$$J = \frac{A^4}{2^{1/\alpha+1}} \frac{\Gamma(1/2\alpha)}{\alpha^{2+1/2\alpha}} \int_0^1 e^{(y-1)/\alpha} (1-y)^{3/2\alpha} (1+y)^{1/2\alpha} dy.$$

In the case of two hydrogen atoms ($\alpha = 1, A = 2$) we obtain the result of Herring and Flicker^[6].

In the case of the atoms of alkaline metals with $\alpha \neq \beta$, we make use of the fact that the values of R which are of interest to us are not very large, and $\alpha - \beta$ is small, so that it becomes meaningful to expand the integral J in powers of $R(\alpha - \beta)$:

$$\begin{aligned} J(\alpha, \beta, R) &= J_0(\alpha, \beta) + R(\beta - \alpha)J_1(\alpha, \beta) \\ &+ 1/2 R^2(\beta - \alpha)^2 J_2(\alpha, \beta). \end{aligned} \quad (10)$$

The values of the integrals J_0, J_1 , and J_2 are given in Table I; the values of the constants A and

Table I

	Value of $10^3 J$	H $\alpha = 1$	Li $\alpha = 0.630$	Na $\alpha = 0.626$	K $\alpha = 0.567$	Rb $\alpha = 0.556$	Cs $\alpha = 0.536$
H $A = 2$	J_0	165	20.1	18.4	8.53	7.12	4.96
	J_1		3.00	2.78	1.63	1.40	1.05
	J_2		3.52	3.21	1.55	1.30	0.92
Li $A = 0.765$	J_0		2.71	2.63	1.26	1.06	0.75
	J_1			$6.5 \cdot 10^{-3}$	$5.4 \cdot 10^{-2}$	$5.4 \cdot 10^{-2}$	0.05
	J_2			0.37	0.144	0.147	0.104
Na $A = 0.751$	J_0			2.50	1.22	1.03	0.72
	J_1				0.05	0.05	0.05
	J_2				0.17	0.14	0.10
K $A = 0.533$	J_0				0.600	0.50	0.36
	J_1					0.004	0.01
	J_2					0.07	0.05
Rb $A = 0.491$	J_0					0.424	0.30
	J_1						0.005
	J_2						0.04
Cs $A = 0.416$	J_0						0.214
	J_1						
	J_2						

Table II

	H	Li	Na	K	Rb	Cs
C	6.5	$1.4 \cdot 10^8$	$1.6 \cdot 10^8$	$3.5 \cdot 10^8$	$3.8 \cdot 10^8$	$5.2 \cdot 10^8$
R_0	7.0	10.4	10.7	13.0	13.4	13.8
$U(R_0), ^\circ\text{K}$	18	350	330	230	210	240

B given in this table have been obtained by joining together the atomic wave functions (4) with those calculated by the Hartree-Fock method. We used the atomic wave functions of alkaline metals, calculated numerically for lithium by Kohn and Rostocker^[8], for sodium by Prokofjew^[9], for K and Cs by Sternheimer^[10,11], and for Rb by Callaway and Morgan^[12].

4. The potential of interaction of two atoms with spin $1/2$ is equal to

$$U_{A,S}(R) = -C/R^6 \pm (E_A - E_S)/2. \quad (11)$$

The first term characterizes the Van der Waals interaction, and the second describes the exchange interaction. A comparison of these terms is shown in Table II. The coefficients C , which determine the interaction of the atoms at large distances, were taken from the paper of Dalgarno^[13]; R_0 is the distance between the atoms (in atomic units), at which the Van der Waals potential (C/R^6) and the exchange-interaction potential $(E_A - E_S)/2$ become equal; $U(R_0)$ is the magnitude of each of these interaction potentials at a distance R_0 , expressed in degrees. As seen from Table II, the exchange interaction is appreciable up to very large distances between nuclei.

5. The cross section for electron exchange,

like the cross section for resonance charge exchange (^[7,14]) is given by the expression $\sigma = \pi R_0^2/2$, where R_0 is the impact parameter of the collision, at which the following relation is satisfied

$$\frac{1}{2} \int_{-\infty}^{+\infty} (E_A - E_S) dt = \frac{11}{40}. \quad (12)$$

Inasmuch as the cross section for electron exchange is much larger than the cross section for elastic scattering, the bending of the trajectories of the relative motion of the nuclei can be neglected, and we can assume that $R^2 = R_0^2 + v^2 t^2$. It follows from (9) that the integral (12) converges rapidly because of the sharp attenuation of the exponential. Therefore the connection between the cross section for electron exchange and the collision velocity is determined by the relation

$$\sigma = \pi R_0^2/2,$$

$$0.22v(\alpha + \beta)^{1/2} = J_0 e^{-(\alpha+\beta)R_0} R_0^{2/\alpha+2/\beta-1, (\alpha+\beta)^{-1/2}}. \quad (13)$$

Of practical interest is the quantity $\langle \sigma v \rangle$, where the averaging is carried out over the Maxwellian distribution of the atoms with respect to the relative velocities. As follows from (13) and (9), in the region $v \sim \langle v \rangle$ we have $(\alpha + \beta) R_0 = \ln(A(v)/v)$, with $A(v)$ weakly dependent on the velocity, so that we can assume it to be constant for each temperature. Using this, we obtain

$$\begin{aligned} \langle v \sigma \rangle &= \langle v \rangle \left[\sigma \left(v = 1.52 \sqrt{\frac{2T}{\mu}} \right) + \frac{0.245}{(\alpha + \beta)^2} \right] \\ &\approx \langle v \rangle \sigma \left(v = 1.52 \sqrt{\frac{2T}{\mu}} \right), \end{aligned} \quad (14)$$

Table III. Cross section for electron exchange (in units of 10^{-16} cm^2).

	Temperature $^\circ\text{K}$	Li	Na	K	Rb	Cs	H
Li	500	89.0	93.2	108	112	118	35.4
	1000	84.7	88.0	103	106	111	33.2
	3000	77.5	81.0	94.4	97.6	102	29.6
Na	500		98.0	117	123	103	36.0
	1000		93.7	111	117	123	34.0
	3000		86.3	102	98	114	30.0
K	500			141	148	158	39.4
	1000			134	142	150	36.7
	3000			125	131	139	32.6
Rb	500				157	168	40.0
	1000				150	160	37.4
	3000				140	149	33.0
Cs	500					180	40.8
	1000					172	38.1
	3000					160	33.8
H	500						19.2
	1000						18.0
	3000						16.0

where μ is the reduced mass of the atoms.

Table III lists the values of $\sigma(T)$ of all possible pairs of the atoms in question, for three values of the temperature (the upper, middle, and lower numbers pertain to 500, 1000, and 3000° K, respectively). The results obtained are in good agreement with the experimental data of Jarrett^[15] for the Rb-Rb pair, and lie within the limits of accuracy of the earlier experiments for the pairs Na - K^[16] and Na - Rb^[17].

The authors are deeply grateful to O. B. Firsov for valuable advice and for interest in the work.

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Translated by J. G. Adashko