RIMENTAL PHYSICS

INSTITUTE OF EXPERIMENTAL PHYSICS

SLOVAK ACADEMY OF SCIENCES

THE 13th SMALL TRIANGLE MEETING on theoretical physics

November 14–16, 2011 | Stará Lesná

Y OF SCIENCES

Influence of Symmetry on the Exchange of One and Two Electrons in Slow Collisions between Protons and Negative Hydrogen Ions

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Abstract

A theoretical investigation is made of one-and two-electron charge exchange in collisions between an atom and an ion of the same element, the latter with two missing electrons. It is shown that the probability of one-electron exchange in the case when the initial term crosses the final ground-state term is half the usual probability for reasons of symmetry: the atom and ion are identical. The occurrence of term crossing in this system alters the physical nature of resonant two-electron exchange. There is a new channel for two-stage exchange of two electrons. The first electron is released on the first pseudocrossing of terms and the second on the second pseudocrossing. In the case of crossing with terms of the excited state, this exchange occurs if the excitation is transferred during the time between the two pseudocrossings. The experimental cross section for the exchange of two electrons in a collision of a negative hydrogen atom with a proton can be ascribed completely to this new channel.

Introduction

Recently at studying slow collisional processes of elementary nuclear systems (H^+, H^-, H_2^+) evidences of an essential role of correlation interaction of electrons were obtained [1]. As a rule ones connect the nature of such correlations with instant Coulomb interaction of electrons by means of the complicated procedure of wave functions symmetrization. However this symmetrization is a consequence of existence of the spin magnetic moments of electrons. An attempt to take into account directly the contribution of spin-spin and retardation interactions of active electrons into cross section of a two-electron charge exchange at slow collision between the negative hydrogen ion and proton is made in the present work.

Besides that we shall consider mutual influence of the exchange of one and two electrons on each other in slow collisions between an atom and an ion of the same

element but with two missing electrons:

$$A+A^{++} \begin{cases} \nearrow & A^+ + A^+, \quad (1a) \\ \searrow & A^{++} + A. \quad (1b) \end{cases}$$

It is found that the symmetry resulting from the fact that the particles A and A^{++} represent the same element has an important influence on the physical nature of these processes and their effective cross sections.

The exchange of one electron, process (1a), is nonresonant and due to the crossing of the energy terms of the initial and final states. The exchange of two electrons is a resonant process and its probability in the absence of one-electron term crossing has already been studied [2, 3]. However, the occurrence of such crossing greatly alters this process.

The absolute magnitude of the term repulsion responsible for the two-electron exchange [3, 4] is considerably less than the splitting in the one-electron exchange. Therefore, when an atom approaches an ion, the one-electron exchange may occur earlier. This would seem to block the two-electron exchange channel (1b) to an extent increasing with the probability of the one-electron exchange during the collision time, i.e., the time interval between two passages of an atom through the same pseudocrossing. In fact, the situation is different. When the probability of the one-electron exchange is high, new ways of exchanging two electrons become possible:

$$A+A^{++} \begin{cases} \nearrow & A^+ + A^+ \to A^{++} + A, \quad (2a) \\ \searrow & A^+ + (A^+)^* \to (A^+)^* + A^+ \to A^{++} + A, \quad (2b) \end{cases}$$

which will be investigated below; it should be noted that the chain of events (2) occurs during the same collision.

Let us assume that, in the process (2b), the probability of a nonadiabatic transition on pseudocrossing of one-electron terms is small. Then, after the first passage of the atom through this pseudocrossing, an electron is very likely (probability ~ 1) to be captured by the ion. If there is no event up to the second passage through the pseudocrossing, the probability of the electron returning to the atom as a result of the second pseudocrossing is equally high and the probability of one-electron charge exchange is low. If excitation is exchanged between the two passages through the same quasicrossing, the first electron can no longer return to the atom since it is now in the ground state. The probability of finding the second electron at the same adiabatic term as the first electron is equally high, i.e., the second electron is transferred to a new atom. This gives rise to the two-electron exchange.

This simple discussion is sufficient to show that, at low collision rates, the effective two-electron exchange cross section of the channel (2b) may be larger than the one-electron charge-exchange cross section or the cross section of the channel (1). This is explained by the relatively large splitting of the terms responsible for the transfer of excitation. For example, when the dipole transition $(A^+)^* \to A^+$,

is allowed for, the splitting decreases proportionally to R^{-3} (R is the internuclear distance), whereas the splitting responsible for the two-electron exchange decreases exponentially [3, 4].

Two-Electron Exchange: Channel (2a)

We shall first consider the case (2a) of the crossing of the terms of the system $A + A^{++}$ with the ground-state term of the $A^+ + A^+$ system, when both A^+ ions are in the ground state. We have to consider here the interaction between three terms: two terms of the $A + A^{++}$ system – the terms even $E_g(R)$ and odd $E_u(R)$ relative to the inversion of the coordinates of the two electrons at the center of the quasimolecule, i.e., at the point which halves the internuclear axis – and one term $E_0(R)$ of the $A^+ + A^+$ system, which has a definite parity, either u or g (it is assumed that the ground state of the A^+ ion is not degenerate). We have to consider only that state of $A^+ + A^+$ whose spin is equal to the spin of the atom A because the total electron spin is conserved in the nonrelativistic approximation. For example, for particles A with two excess electrons (in addition to those in the filled shells), the spin of two electrons is either zero or unity. Consequently, in the $A^+ + A^+$ system, we have to consider either the singlet or triplet states, and the singlet state is even relative to inversion at the center of the quasimolecule, whereas the triplet term is odd. The odd state is described by all the formulas given below if g is exchanged with u; all the conclusions still apply to this case.

In general, the triplet state of the $A^+ + A^+$ system, which is odd relative to inversion, also interacts with the odd state of the $A+A^{++}$ system. This interaction is of the spin-orbit type; it is weak and we shall ignore it for large interatomic distances.

The initial conditions correspond to an $A + A^{++}$ collision:

$$\Psi(\vec{r}_1,\vec{r}_2,t) \xrightarrow[t\to-\infty]{} \frac{1}{\sqrt{2}}\left[\Psi_g(\vec{r}_1,\vec{r}_2)e^{-i\int\limits_{-\infty}^{t}E_g dt'} + \Psi_u(\vec{r}_1,\vec{r}_2)e^{-i\int\limits_{-\infty}^{t}E_u dt'}\right]. \quad (3)$$

The quasimolecular functions $\Psi_{g,u}$ reduce, in the limit $R \to \infty$, to combinations of the atomic functions $\Psi_{a,b}$ corresponding to the case when both electrons are near the nucleus a or b:

$$\Psi_{g,u} = [\Psi_a(\vec{r}_1,\vec{r}_2) \pm \Psi_b(\vec{r}_1,\vec{r}_2)]/\sqrt{2}. \quad (4)$$

Let ω be the probability of a nonadiabatic transition for a single passage through a pseudocrossing. Subject to the initial condition (3), the wave function is then

$$\Psi(\vec{r}_1,\vec{r}_2,t) \xrightarrow[-t_1<t<+t_+]{} \left(\frac{\omega}{2}\right)^{1/2}\Psi_g(\vec{r}_1,\vec{r}_2)e^{-i\int\limits_{-\infty}^{t}E_g dt'} +$$

$$+\left(\frac{1-\omega}{2}\right)^{1/2}\Psi_0(\vec{r}_1,\vec{r}_2)e^{-i\int\limits_{-\infty}^{-t_1}E_g dt' - i\int\limits_{-t_1}^{t}E_0 dt'} + \frac{1}{\sqrt{2}}\Psi_u(\vec{r}_1,\vec{r}_2)e^{-i\int\limits_{-\infty}^{t}E_u dt'}. \quad (5)$$

Here, $\pm t_1$ are the moments of passage through a pseudocrossing.

Similarly, if we consider the system passing through a pseudocrossing at a time $+t_1$ when the particles fly apart, we obtain the probability of the two-electron exchange during the whole collision ($A + A^{++} \to A^{++} + A$):

$$P_2 = \sin^2\left(\frac{\chi_1 - \chi_2}{2}\right) + \omega^2 \sin^2\frac{\chi_1}{2} + \omega\left[\sin\left(\frac{\chi_1 + \chi_2}{2}\right)\sin\left(\frac{\chi_1 - \chi_2}{2}\right) - \right.$$
$$\left. - \sin^2\left(\frac{\chi_1 - \chi_2}{2}\right)\right], \quad (6)$$

where the phases $\chi_{1,2}$ are

$$\chi_1 = \int_{-t_1}^{+t_1} (E_0 - E_g)\, dt', \qquad \chi_2 = \int_{-\infty}^{+\infty} (E_u - E_g)\, dt'. \quad (7)$$

The phase χ_2 determines the contribution of a simultaneous jump of two electrons. If this phase is small, Eq. (6) reduces to

$$P_2 \approx (1 + \omega^2)\sin^2\left(\frac{\chi_1}{2}\right); \quad \chi_2 \ll \chi_1. \quad (8)$$

The interference phase χ_1, is large if it is governed by the Coulomb displacement of the term E_0: $E_0 - E_g \sim R^{-1}$ i f the crossing occurs in the asymptotic range of large interatomic distances. Therefore, averaging Eq. (8) over a small interval of the impact parameters $\Delta\rho$, we find that

$$\overline{P}_2 \approx \frac{1}{2}(1 + \omega^2). \quad (9)$$

When the probability of a nonadiabatic transition is $\omega \to 0$, the formulas (8) and (9) reduce to

$$P_2 \approx \sin^2\left(\frac{\chi_1}{2}\right), \quad (10)$$

$$\overline{P}_2 \approx \frac{1}{2}. \quad (11)$$

In the limit $\omega \to 0$, the even component of the $A + A^{++}$ system most probably follows the adiabatic term $E_g \to E_0 \to E_g$.In this case, the dephasing of the quasimolecular g and u states and the exchange of two electrons are governed only by the phase difference $E_0 - E_g$, which is reflected in Eq. (10).

The probability P_1 of the one-electron charge exchange throughout the whole collision is

$$P_1 = \omega(1 - \omega)[1 + \cos\chi_1]. \quad (12)$$

Averaging this expression over the small interval $\Delta\rho$, we obtain

$$\overline{P}_1 = \omega(1 - \omega). \quad (13)$$

This quantity is half the usual value because, in the symmetric $A+A^{++}$ case, half the colliding atoms are in the noninteracting state Ψ_u.

If $\omega \to 1$, the system jumps a pseudocrossing without being affected by it and then the probability of the twoelectron charge exchange (6) tends to the earlier value [2, 3, 4]:

$$P_2 \xrightarrow[\omega\to 1]{} \sin^2\left(\frac{\chi_2}{2}\right). \tag{14}$$

It follows from Eqs. (10) and (11) that, in the case of adiabatically low collision rates so that $\omega \to 0$, the effective cross section for the two-electron exchange is $\sigma_2 \to \pi R_1^2/2$ (R_1 is the pseudocrossing radius) and it is greater than even the maximum one-electron charge exchange cross section to the ground state, irrespective of the term splitting $\Delta E_1 = E_g - E_u$, responsible for the two- electron exchange.

We can thus see that the symmetry of the molecules formed as a result of a collision has a considerable influence on the probabilities of exchange of one and two electrons.

The above results are derived on the assumption that the laws governing the changes in the phases of the adiabatic states, i.e., the functions $E(t)$, change precisely at the pseudocrossing moments $\pm t_1$. This is justified if the size of the region where the exact adiabatic terms differ greatly from the unperturbed terms is small compared with R_1. This condition is satisfied if the repulsion of terms in a pseudocrossing is small compared with $E_0 - E_{g,u}$ for $\rho \lesssim R_1$, which is clearly valid because $E_0 - E_{g,u} \sim R^{-1}$ and the repulsion of the terms is exponentially small for large values of R_1.

Two-Electron Exchange: Channel (2b)

We shall now consider the case (2b) when the terms of the initial system cross the terms of the $A^+ + (A^+)^*$ excited states. In this case, the atomic particles are in different states and, therefore, quasimolecular states are always degenerate relative to inversion, i.e., there are always even and odd states with the same energy in the limit $R \to \infty$ (even if the atomic excited state $(A^+)^*$ is not itself degenerate).

Let us assume that the atomic excited state $(A^+)^*$ is not degenerate. Applying the above procedure, we obtain the probability of the two-electron exchange:

$$P_2^{(*)} = \omega^2 \sin^2\left(\frac{1}{2}\int_{-\infty}^{+\infty} \Delta E_1 dt'\right) + (1-\omega)^2 \sin^2\left[\int_{-\infty}^{-t_1} \Delta E_1 dt' + \frac{1}{2}\int_{-t_1}^{t_1} \Delta E_2 dt'\right], \tag{15}$$

where ΔE_2 is the splitting of the terms responsible for the excitation transfer $A^+ + (A^+)^* \to (A^+)^* + A^+$, which occurs during the motion of the particles between two pseudocrossing moments $\mp t_1$. It is assumed that the splittings $E_g - E_u$ are much smaller than the matrix element of the one-electron exchange, so that the repulsion of the terms and the probability of the one-electron transition ω are the same for the g and u states. Averaging the interference terms has already been carried out in Eq. (15).

We shall now consider the above expressions for the charge-exchange probabilities. The first term in Eq. (15) is the probability of direct charge exchange in accordance with Eq. (1a). It is ω^2 times smaller than the usual probability because of the presence of the one-electron charge-exchange channel. In the range of adiabatically low rates $\omega \to 0$, even the direct channel is closed. However, a second channel then opens up: the second term in Eq. (15) becomes more important. This second channel is also important for $\omega \sim 1 - \omega$ because the splitting of the terms resulting in excitation transfer is usually greater than the two-electron exchange splitting $|\Delta E_2| > |\Delta E_1|$.

In the general case of crossing with N terms of the $A+A^{++}$ system, the formula (15) becomes

$$P_2^N = \omega_1^2\omega_2^2 \ldots \omega_N^2 \sin^2\left(\frac{1}{2}\int_{-\infty}^{+\infty} \Delta E_1 dt'\right) + \\ + \sum_{k=1}^{N} \omega_1^2\omega_2^2 \ldots \omega_{k-1}^2 (1-\omega_k)^2 \sin^2\left[\int_{t_k}^{\infty} \Delta E_1 dt' + \frac{1}{2}\int_{-t_k}^{t_k} \Delta E_2^{(k)} dt\right]. \qquad (16)$$

Two-Electron Exchange between Proton and Negative Hydrogen Ion

We shall now consider the case of a collision of a negative hydrogen atom with a proton, $H^- + H^+$, for which the two-electron charge-exchange cross section was determined experimentally [1] in the relative energy range 50-190 eV or at relative velocities $v \approx 1.5 - 2.5 \times 10^7$ cm/sec ($\approx 0.07 - 0.12$ a.u.). For this case, using the generalized Breit operator [8, 7, 8, 9, 10] the term splitting of the direct channel is

$$\Delta E_1 \approx 7.9 \times 10^{-7} R^{3.49} e^{-0.47R}\left(1 - \frac{3\omega_0^2 R^2}{2c^2}\right). \qquad (17)$$

This expression has a maximum at $R \approx 7.4$ and its value is then $\Delta E_1(7.4) = 2.7 \times 10^{-5}$ a.u. Such small splitting means that, even if the direct charge exchange does occur, this will happen outside the asymptotic range of the interatomic distances.

We shall now estimate the probability product $\omega_1^2\omega_2^2 \ldots \omega_N^2$, which occurs in the first term of (16), and which represents the probability of the evolution of the system in accordance with the channel (2b). The ionic term $H^- + H^+$ crosses three terms of the $H(1s) + H*(n)$ system with $n = 4, 3$ and 2. According to the δ-potential model of a negative ion, the charge exchange occurs only to one of the n^2 degenerate states [13]. Splitting of the terms $\delta E_n(R) = 2\Delta E_n(R)$ in the quasicrossing points $R_n = Z/(\varepsilon_0 - E_n)$ is

$$\delta E_n(R) = 4\pi N_0 \sqrt{Q_n(R)}, \quad N_0 = \sqrt{\frac{\gamma}{2\pi}}, \quad \varepsilon_0 = -\frac{\gamma^2}{2},$$

$$Q_n = \sum_{l=0}^{n-1} \sum_{m=-1}^{l} |\psi_{nlm}(R)|^2 = (\phi'_{n0}(R))^2 + 2\left(E_n + \frac{Z}{R}\right)\phi_{n0}^2(R), \qquad (18)$$

where ε_0 is the binding energy of external electron in unperturbed negative ion, and $E_n = -Z^2/2n^2$ are Coulomb energy levels of H-like ion with nuclear charge Z. The function ϕ_{n0} can be expressed through the confluent hypergeometric function:

$$\phi_{n0}(\tau) = \sqrt{\frac{Z}{4\pi n}}\tau \exp\left(-\frac{\tau}{2}\right) F(-n+1, 2, \tau). \tag{19}$$

Values of terms splitting $\delta E_n(R)$ in the quasicrossing points R_n for considered system $H^- + H^+$ are given in Table 8. The crossing with $n = 4$ level can be ignored as too distant: $R_n = 283.005$ a.u. We shall estimate the probabilities ω_3 and ω_2 using the Landau-Zener model:

$$\omega_n = \exp\left[-\frac{\pi}{2}\frac{R^2\delta E_n^2}{v}\right]. \tag{20}$$

Using the parameters R_n and δE_n represented in Table 8, we have

$$\omega_3 = 0.993, \quad \omega_2 = 0.074$$

for the case when the radial velocity is $v_{rad} \approx v = 0.1$ a.u.

Table 8: The radiuses of the Coulomb orbits $r_n = 2n^2/Z$, positions of quasicrossings R_n and splittings $\delta E_n(R_n) = 2\Delta E_n(R_n)$ of terms for the system $H^- + H^+$.

n	r_n, a.u.	R_n, a.u.	$\delta E_n(R_n)$, a.u.
1	2.0	2.117	1.652×10^{-1}
2	8.0	10.279	1.876×10^{-2}
3	18.0	35.921	2.318×10^{-4}
4	32.0	283.005	7.123×10^{-27}

If the phase difference required for the direct chargeexchange process is accumulated at $\rho \sim 1$ a.u. (or $\sim a_0$, which is the Bohr radius), then, subject to allowance for weakening by a factor $\omega_2^2\omega_3^2 = 5.5 \times 10^{-3}$, we can estimate the contribution of the direct channel (1b) to the total two-electron charge-exchange cross section, which gives the value $\sigma_1(v = 0.1) \lesssim 5 \times 10^{-19}$ cm^2, two orders of magnitude less than the experimental cross section: $\sigma_{exp}(v = 0.1) \approx (4 \pm 2) \times 10^{-17}$ cm^2. Consequently, in this case, the whole cross section is governed by the second channel.

We shall now estimate the cross section for the two-electron exchange $H^- + H^+ \to H^+ + H^-$, in accordance with the second channel (2b) for the case when $v = 0.1$ and we shall do this using the second term of Eq. (15). The contribution of the term $H^*(n = 3, \omega_3 \approx 0.993)$ can be ignored and allowance need only be made for the crossing with the term $H^*(n = 2)$, which is characterized by $(1 - \omega)^2 \approx 1$. We can then see that the probability of the two-electron exchange is simply equal to the probability of the exchange of excitation in a time between $-t_1$ and $+t_1$:

$$P_2^{(*)} \approx \sin^2\left(\frac{1}{2}\int_{-t_1}^{t_1} \Delta E_2 dt\right). \tag{21}$$

The application of Eq. (15) to the case under consideration requires further discussion because the excited states $H^*(n)$ are degenerate. This application is possible if there is no mixing of the degenerate states and this will be assumed here. The probability (21) becomes ~ 1 for the impact parameters $\rho < R_2 = 10.279a_0$ (the trajectory is assumed to be rectilinear), so that

$$\Delta E_2 = \frac{2|d_{12}|^2}{R^3}\left(1 + \frac{\omega_0^2 R^2}{2c^2}\right), \tag{22}$$

$$\frac{1}{2}\int_{-t_1}^{t_1} \Delta E_2 dt \lesssim \frac{|d_{12}|^2}{v\rho^2}\int_{-\infty}^{\infty} \frac{d\xi}{(1+\xi)^{3/2}} = \frac{2|d_{12}|^2}{v\rho^2}, \tag{23}$$

where $|d_{12}|^2$ is the square of the matrix element of the dipole moment: $|d_{12}|^2 = |\langle\Psi_{1s}|r\cos\theta|\Psi_{2p_0}\rangle|^2 = 0.551$ for the $2p_0 \to 1s$ transition in the hydrogen atom. Estimating the cross section from $\sigma \sim \pi\rho_0^2/2$, where ρ_0 is the impact parameter for which the phase (21) becomes equal to $\pi/2$, we obtain $\sigma(v = 0.1) \approx 3 \times 10^{-16}$ cm^2 ($\rho_0 \approx 2.6$). The degenerate states are most likely to be mixed in the $\rho \sim \rho_0$ case, so that the probability of charge exchange decreases by a factor of n^2. We then obtain $\sigma \sim 7.5 \times 10^{-17}$ cm^2, which is close to the experimental value $(4 \pm 2) \times 10^{-17}$ cm^2. These estimates indicate that the two-electron exchange $H^- + H^+ \to H^+ + H^-$ does indeed occur in accordance with the channel (2b). The exact theoretical value of the cross section can be obtained by solving the many-level problem.

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