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ROLE OF INNER SHELLS IN CHARGE-EXCHANGE BETWEEN PROTONS AND MULTIELECTRON ATOMS

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Charge exchange between protons and complex atoms leading to the formation of hydrogen atoms in different n and l states is discussed. It is shown that at sufficiently high collision energies in such reactions, it is necessary to take into account electron capture from the inner shells. Calculations are reported of the cross sections for the formation of highly excited hydrogen atoms produced during charge exchange between protons and alkali-metal atoms. Total charge-exchange cross sections are also reported for Cs and Ar atoms. The calculations are shown to be in agreement with experimental data.

1. INTRODUCTION

WHEN charge-exchange reactions between protons and atoms, e.g., reactions of the form $H^+ + A \rightarrow H(n, l) + A^+$, where n and l are the quantum numbers of the final hydrogen atom, are investigated, there is practical interest not only in the total number of neutral hydrogen atoms that are produced, but also in their distribution over the excited states. A considerable number of experimental papers have been published in recent years in this field, and a number of interesting features of the charge-exchange process have been discovered. For example, it is shown in [1, 2] that the cross section for the charge-exchange between protons and inert-gas atoms, leading to the formation of excited hydrogen atoms, has two peaks. At the same time, it is well known that the cross section for charge exchange ending in the ground state has only one maximum when plotted as a function of energy. According to [3], the second peak is due to the interference between the transition amplitudes in the first- and second-order perturbation theory in which the ground state of the resulting hydrogen atom acts as a virtual level.

There is another feature which is characteristic for charge exchange on multielectron atoms and cannot be explained within the framework of the three-body model. This is the break on the curve showing the cross section as a function of energy, which is followed by the unusually slow (for such reactions) decrease of the cross section with increasing energy [the high-energy part of this curve usually follows the law $\sigma(E) \sim E^{-6}$ or E^{-7}]. This phenomenon has been observed for charge exchange between protons and alkali-metal atoms resulting in highly excited hydrogen atoms with $n \approx 10$–16 [4] and those with $n = 2$.[5] The reason for this behavior of the cross section is connected with the possible capture of electrons from the inner shells of the target atoms. This has been reliably demonstrated in the case of highly excited hydrogen atoms by Il'in et al.,[4] who compared the charge-exchange cross sections for alkali metals and inert gases which have similar inner shell structures. Preliminary calculations of the cross sections for the production of hydrogen atoms in the 2s state during charge exchange between protons and alkali-metal atoms[6] have also shown that satisfactory agreement between theoretical and experimental data can be achieved only when capture from the inner shells is taken into account. If, however, the target atoms are, say, those of argon instead of the alkali metals, the inner shells have practically no effect up to energies of the order of a few hundred keV.[6] One would therefore expect that the contribution of the inner shells depends on the structure of the target atom and is very sensitive to the collision energy.

This paper is devoted to charge exchange between protons and target atoms, leading to the formation of hydrogen atoms in the ground and excited states. It is shown that at sufficiently high collision energies the inner shells always provide a greater contribution than the optical electrons. The energy region where the inner electrons begin to play a part is very dependent on the structure of the atom. A considerable discrepancy between theory and experiment is obtained unless the inner shells are taken into account. All this is valid both for the cross sections for the formation of hydrogen atoms with definite n and l and for the total charge charge-exchange cross sections.

We shall consider alkali-metal and inert-gas atoms as the targets for the charge-exchange reactions. Our calculations will be based on a simple modification of the Born approximation, namely, the Brinkman–Kramers (BK) approximation. The basic formulas are given in Sec. 2 and some general features of the BK approximation, which are independent of the specific form of the atomic wave functions, are discussed. Hydrogen-like wave functions are then used to obtain analytic expressions for qualitative estimates of the contribution of the inner shells to charge exchange leading to the formation of highly excited hydrogen atoms. In Sec. 3 numerical calculations based on more accurate wave functions are compared with experimental data. In all the cases considered below the inner shells provide an important contribution.

2. BASIC FORMULAS

Suppose that the collision between a proton and an atom A results in the capture of an electron from a shell containing N equivalent electrons:

$$H^+ + A(n_0l_0^N) \to H(n,l) + A(n_0l_0^{N-1}), \tag{1}$$

where $n_0 l_0$ and nl are the quantum numbers of the captured electron and the resulting hydrogen atom.

The cross section for the reaction given by Eq. (1) may be written in the form[1)]

$$\sigma = \pi a_0^2 \frac{N}{2\pi^2 v^2} \int_{k_0-k_1}^{k_0+k_1} |f(\mathbf{q})|^2 q\,dq, \tag{2}$$

where v is the relative velocity, $\mathbf{k}_0$ and $\mathbf{k}_1$ are the relative momenta before and after the collision, and $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_1$ is the momentum transfer.

The scattering amplitude $f(\mathbf{q})$ in the BK approximation is of the form (see, for example, [7]):

$$f(\mathbf{q}) = \int \Psi_1^*(\mathbf{r}')\, e^{-i\varkappa\mathbf{r}'}\, V^{BK}\, \Psi_0(\mathbf{r})\, e^{i\alpha\mathbf{r}}\, d\mathbf{r}\, d\mathbf{r}', \tag{3}$$

where Ψ_0, Ψ_1 are the wave functions of the electron in the atom A and the hydrogen atom, respectively. The vectors $\boldsymbol{\kappa}$ and $\boldsymbol{\alpha}$ are related to $\mathbf{q}$ and $\mathbf{v}$ by the following formulas:

$$\varkappa = \mathbf{q} + \frac{M_A}{M_A + M}\mathbf{v}, \quad \alpha = \mathbf{q} - \frac{M}{M_A + M}\mathbf{v}; \tag{4}$$

where M_A and M are the masses of the atom and proton, respectively. Moreover, conservation of energy yields

$$\varkappa^2 - \alpha^2 = \omega, \tag{5}$$

where $\omega = I - 1/n^2$ and I is the ionization potential of the l_0^N shell. Equations (4) and (5) are valid to within terms of the order of 1/M.

The potential V^{BK} in Eq. (3) is usually represented by the so-called post and prior approximations

$$V_f = \zeta(r)/r, \tag{6a}$$

$$V_i = 1/r'; \tag{6b}$$

where $\zeta(r)$ is the effective charge of the atomic residue. In the case of the hydrogen atom $\zeta(r) = 1$ and it may be shown[7] that the use of either V_f or V_i leads to the same result. In the case of charge exchange on multielectron atoms, on the other hand, we have $\zeta(r) \neq 1$ and there is the well-known discrepancy between the cross sections calculated on the post and prior approximations (see, for example, [12]).

Substituting Eqs. (6a) and (6b) in Eq. (3), and summing Eq. (2) over the magnetic quantum numbers, we obtain the following expression for the total cross section for capture into the n, l state:

$$\sigma(n_0l_0 - nl) = \pi a_0^2 \frac{8N(2l+1)}{v^2} \int_{\varkappa_{min}}^{\infty} P^2(\varkappa) Q^2(\sqrt{\varkappa^2 - \omega})\,\varkappa\, d\varkappa, \tag{7}$$

$$\varkappa_{min} = |\omega/2v + v/2|.$$

The functions P and Q are given by the following formulas:

1) in the post approximation

$$P_f = \int_0^\infty R_{nl}^{H}(r)\, j_l(\varkappa r)\, r^2\, dr, \tag{8a}$$

$$Q_f = \int_0^\infty R_{n_0l_0}(r)\, j_{l_0}(r\sqrt{\varkappa^2 - \omega})\, \zeta(r)\, r\, dr; \tag{8b}$$

2) in the prior approximation

$$P_i = \int_0^\infty R_{nl}^{H}(r)\, j_l(\varkappa r)\, r\, dr, \tag{9a}$$

$$Q_i = \int_0^\infty R_{n_0l_0}(r)\, j_{l_0}(r\sqrt{\varkappa^2 - \omega})\, r^2 dr, \tag{9b}$$

where R_{nl} are the radial wave functions and $j_l(r)$ is the spherical Bessel function; the superscript H represents the hydrogen atom.

The derivation of Eq. (7) involves the replacement of integration with respect to q by integration with respect to κ so that the integrand in Eq. (7) turns out to be independent of the velocity v. This substantially simplifies our calculations.

There is practical interest in the cross sections for capture into the highly excited states of the hydrogen atom, but one is usually not interested in the distribution of the hydrogen atoms over the values of the orbital quantum number l.

The above cross sections can readily be obtained by summing Eq. (7) over l and using the well-known properties of the hydrogen-like wave function[8]

$$\sigma(n_0l_0 - n) = \sum_l \sigma(n_0l_0 - nl) = \pi a_0^2 \frac{8N}{v^2} \int_{\varkappa_{min}}^{\infty} P_n^2(\varkappa) Q^2(\sqrt{\varkappa^2 - \omega})\,\varkappa\, d\varkappa. \tag{10}$$

The quantity Q is given by Eqs. (8b) and (9b), as before, and $P_n(\kappa)$ is of the form

$$P_{nf} = \frac{2^2}{n^{3/2}} \frac{1}{(\varkappa^2 + n^{-2})^2}, \quad P_{ni} = \frac{2}{n^{3/2}} \frac{1}{(\varkappa^2 + n^{-2})}. \tag{11}$$

It follows from Eqs. (10) and (11) that the quantity $n^3\sigma(n_0 l_0 - n)$ is independent of n for large values of n, and is given by the following expressions:

1) in the post approximation

$$n^3\sigma(n_0l_0 - n) = \pi a_0^2 \frac{8N}{v^2} \int_{\varkappa_{min}}^{\infty} \frac{2^4}{\varkappa^8} Q_f^2(\sqrt{\varkappa^2 - \omega})\,\varkappa\, d\varkappa, \tag{12a}$$

2) in the prior approximation

$$n^3\sigma(n_0l_0 - n) = \pi a_0^2 \frac{8N}{v^2} \int_{\varkappa_{min}}^{\infty} \frac{2^2}{\varkappa^4} Q_i^2(\sqrt{\varkappa^2 - \omega})\,\varkappa\, d\varkappa. \tag{12b}$$

Let us now consider some general properties of the charge-exchange cross section within the framework of the BK approximation given by Eq. (7). At high velocities ($v > \sqrt{|\omega|}$) the lower limit of integration in Eq. (7) is proportional to v (in fact, $\kappa_{min} \sim v/2$). In this case, the cross section is determined by the rate of decrease of the integrand for large κ which, in turn, is determined by the properties of the atomic wave functions for small $r \sim 1/\kappa$. The Fourier transform of the wave function falls at least as slowly as $1/\kappa^4$, which means that at high velocities $\sigma(v) \sim v^{-m}$, $m \geq 12$. The lower limit of integration in Eq. (7) is a minimum for $v = \sqrt{|\omega|}$, and this value of the velocity fixes the position of the maximum of the product σv^2. Further reduction in velocity ($v < \sqrt{|\omega|}$) ensures that the lower limit of integration in Eq. (7) begins to increase again ($\kappa_{min} \sim |\omega|/2v$), and the cross section falls to zero ($\sigma(v) \sim v^m$, $m \geq 8$). Because of this rapid variation in the

1)We are using the atomic system of units with the energy expressed in terms of the Rydberg.

cross section with velocity, the cross-section peak lies near the maximum of σv^2, i.e., in the region $v \sim \sqrt{|\omega|}$.

Let us now estimate the contribution to the total charge-exchange cross section due to different shells, using the hydrogen-like wave functions for the atomic functions $R_{n_0 l_0}$ [2)]

$$R_{n_0l_0}(r) = (Z^*)^{3/2} R^{\mathrm{H}}_{n_0l_0}(Z^* r), \tag{13}$$

where $Z^* = n_0 I^{1/2}$ is the effective charge.

In this approximation all the calculations can be carried out analytically. For the sake of simplicity, we shall confine our attention to capture into a highly excited state n (when $\omega \sim I$) and the prior approximation given by Eq. (12b) for $n^3\sigma$. For two filled shells with binding energies I_1 and I_2 ($I_1 > I_2$) the ratio of cross sections summed over l_0 is

$$\frac{\sigma_1}{\sigma_2} = \frac{n_1{}^2}{n_2{}^2}\alpha^{-15/2}\left(\frac{1+x}{1+x/\alpha}\right)^{10}, \quad x = \frac{v^2}{I_2}, \quad \alpha = \frac{I_1}{I_2} > 1. \tag{14}$$

We readily verify with the aid of Eq. (14) that in all real cases the main contribution at low energies is due to the shell with the lower ionization potential, i.e., $\sigma_1 \ll \sigma_2$. At high energies we have the opposite situation. In the limiting case of high and low energies the cross-section ratio is determined by the ratio of the ionization potentials

$$\frac{\sigma_1}{\sigma_2} \approx \begin{cases} (n_1{}^2/n_2{}^2)\,\alpha^{-15/2}, & v^2 \ll I_1. \\ (n_1{}^2/n_2{}^2)\,\alpha^{5/2}, & v^2 \gg I_1. \end{cases} \tag{15}$$

It may be shown that, for any α, an inner shell begins to provide an important contribution in the energy range where the cross section for capture from the shell reaches a maximum, i.e., when $v^2 \sim I$.

As already noted, for $v^2 \gg I$ and $v^2 \ll I$ the cross section is determined by the behavior of the Fourier transform of the atomic wave function for large κ. Hence, it is clear that the main contribution to the cross section in these regions is due to s electrons. The formula for σ_1/σ_2 given by Eq. (15) will retain its form to within a weighting factor even if shell 2 is identified with the optical electron of an alkali metal. When $v^2 \sim I_1$ the formula given by Eq. (14) gives values of σ_1/σ_2 for an alkali-metal atom which are much too low since σ_2 in Eq. (14) includes the contribution of electrons with $l_0 \neq 0$, and these are not, in fact, present. It is clear from the above estimates that for an arbitrary atom and sufficiently high energies the inner shells provide the main contribution to the cross section.

The results summarized in the present section were obtained mainly with the aid of hydrogen-like wave functions which, in general, are satisfactory only for large r. Since large κ, i.e., small r, are important in the charge-exchange problem, no final conclusion about the contribution of the inner shells can be drawn unless the calculations are made with more accurate wave functions.

3. NUMERICAL CALCULATIONS

The charge-exchange cross-section calculations were carried out on the BÉSM-4 computer in the BK approximation, using Eqs. (7), (8), and (12a). For the functions R_{nl} we used semi-empirical functions obtained by solving the Schrödinger equation with the experimental value of the energy. The potential $\zeta(r)/r$ was calculated using the nodeless Slater functions (see [10]).

All our figures give the cross sections calculated in the post approximation, which results in better agreement with experiment than the prior approximation (especially near the cross section maximum). The charge-exchange cross section is very sensitive to I (electron separation energy) which varies substantially within a shell with given n_0 as the orbital quantum l_0 is varied. Subshells with different l_0 must therefore be considered separately. The values of I for inner electrons which we used in our calculations are given in the table.

Values of the Ionization Potential I (eV)

Li	Na	K	Rb	Cs	Ar
$2s^2$ — 65	$2p^6$ — 38 $2s^2$ — 63	$3p^6$ — 24 $3s^2$ — 34	$4p^3$ — 21 $4s^2$ — 29	$5p^6$ — 17 $5s^2$ — 23	$3s^2$ — 35 $2p^6$ — 246 $2s^2$ — 320

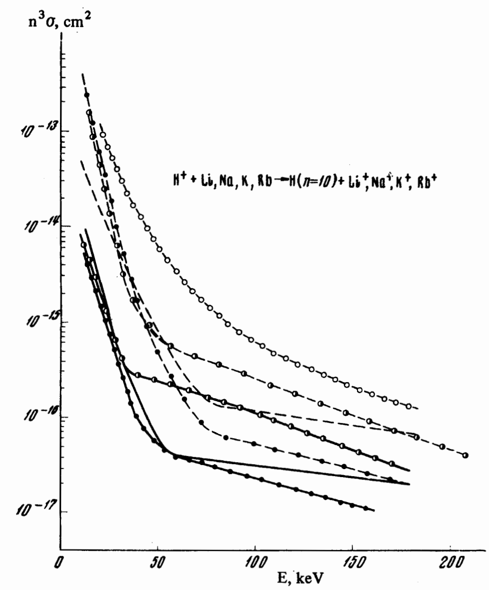

FIG. 1. Cross sections for charge exchange between protons and alkali metals: ●—Li; curve without points—Na; ◐—K; ○—Rb. Solid curves—experimental, [4] broken curves—experimental data obtained in this work.

Figures 1 and 2 show the experimental and theoretical cross sections with allowance for the inner shells for the charge exchange between protons and alkali-metal atoms, leading to the formation of highly excited hydrogen atoms (n = 10). Figure 2 illustrates the effect of inner shells in the case of cesium atoms. It is clear that from E ~ 20 keV onward the 6s shell has practically no effect, and the capture of 5s and 5p electrons is much more likely. In this energy region the $n_0 = 4$ shell does not as yet contribute. A similar situation occurs for other alkali metals.

A common property of alkali metals and inert gases is that the cross sections for the capture of inner electrons with quantum numbers $n_0 l_0$ provide equal contributions and, therefore, at high energies the products $n^3\sigma$ behave in a similar fashion. The nearest inner

2) Functions of this kind were used for charge-exchange calculations in [9].

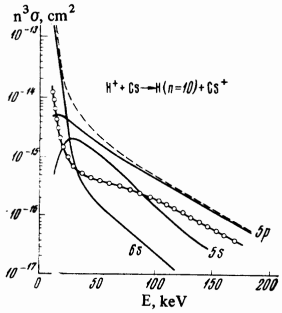

FIG. 2. Cross section for charge exchange between protons and Cs atoms. Solid curves—cross sections for the capture of electrons from different Cs shells, broken curve—total cross section, points—experimental. [4]

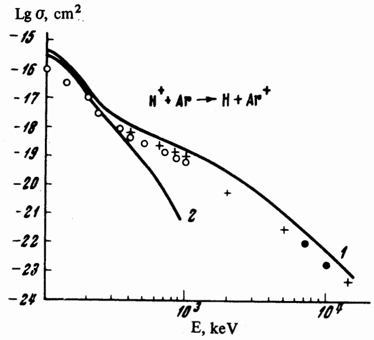

FIG. 4. Total cross section for the charge exchange between protons and argon atoms. 1—Inner shells allowed for; 2—inner-shell contribution neglected; O—[16], ●—[17], + [18] experimental data.

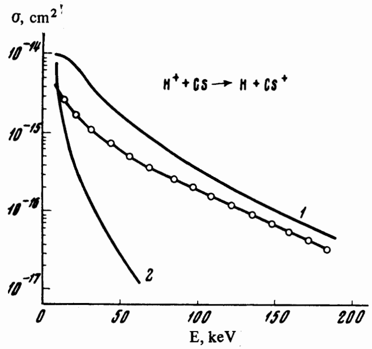

FIG. 3. Total cross section for charge exchange between protons and cesium atoms. 1—Inner shells allowed for; 2—inner shell contribution neglected; points—experiment. [4]

shells of inert gases provide a contribution beginning with $E \sim 300-500$ keV. There are no experimental data on $n^3\sigma$ in this energy range, but theoretical calculations are reported in [11]. At low energies the cross sections are quite different because the weakly bound optical electron of the alkali metal (see Fig. 2) plays a part in the process. Calculations confirm this interpretation of the experiments.[4]

The total cross sections for the formation of hydrogen atoms are also affected by the inner-shell contributions. Figures 3 and 4 show the total cross sections for the formation of hydrogen atoms during charge exchange between protons and cesium and argon atoms. These cross sections were calculated with and without allowance for the inner shells. The main contribution to the total cross section is due to charge exchange to the 1s, 2s, and 2p states. Analysis of the calculated cross sections confirms the fact that (see Section 2) for reactions with a resonance defect $\omega = I - 1/n^2$ the cross sections for capture from a shell with ionization potential I reach a maximum for $v_m \sim \sqrt{|\omega|}$ or, more precisely, when $v_m = 0.7\sqrt{|\omega|}$, which is valid to a good degree of accuracy.

It is well known that comparison of calculations based on the BK approximation with the results obtained by more precise methods and with experimental data on charge exchange between protons and hydrogen and helium atoms have shown that the cross sections obtained by the BK approximation are too high at all energies.[12] It is clear from Figs. 3 and 4 that when only the optical electrons are taken into account we have the opposite situation, namely, the theoretical results lie below the experimental curves. This also indicates that the inner shells must be taken into account in the case of multi-electron atoms.

We note that the inner-shell electrons may be important not only in charge exchange but also in other atomic processes. For example, the direct detachment of inner-shell electrons and their excitation to self-ionization levels leads to a substantial increase in the cross sections of complex atoms[12] and multiply charged ions[14] for ionization by electron impact. These processes are also responsible for the structural features on the ionization functions of alkali-earth elements reported in [15]. However, in contrast to charge exchange, the contribution due to the inner shells is not as clearly defined because of the slower reduction in the ionization cross sections at high energies. It will be sufficient to note that, whereas in the case of ionization the inner shells tend to increase the cross section by a moderate factor, in the case of charge exchange the capture of inner-shell electrons may increase the cross section by a few orders of magnitude.

CONCLUSION

Our conclusion is that both inner and outer shell electrons must be taken into account in calculations of the cross sections for charge exchange on complex atoms. When the inner-shell electrons are neglected, the discrepancy between theory and experiment is much greater than the standard error of the BK approximation, and has a different sign (see Figs. 3 and 4). It would therefore be interesting to perform a direct experiment in which the state of the target can be determined after the collision, since this would enable us directly to compare the theoretical and experimental cross sections for capture from inner shells.

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