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RESONANCE CHARGE EXCHANGE IN COLLISIONS OF ALKALI METAL ATOMS

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A general relationship is established between the cross section for resonance charge exchange in a slow collision of an ion with its parent atom and the asymptotic form of the radial wave function of an electron in the atom. The velocity dependence of the resonance charge-exchange cross section for alkali metal atoms is compared with experiment.

1. The cross section for resonance charge exchange between a slow ion and its parent atom is $\sigma = \pi R_0^2/2$, where R_0 is given by the relationship[1,2]

$$\int_{R_0}^{\infty}\frac{[\varepsilon_u(R)-\varepsilon_g(R)]R\,dR}{v\sqrt{R^2-R_0^2}}=\frac{11}{40}. \tag{1}$$

Here $\epsilon_u - \epsilon_g$ is the splitting of the energy level of an atomic electron under the action of the ion, v is the relative velocity of the colliding nuclei, and R is the distance between the nuclei. We shall use the system of atomic units with $\hbar = m_{el} = e^2 = 1$. Since, for slow collisions, the resonance charge-exchange cross section is large, to determine it it is sufficient to know the asymptotic form of $\epsilon_u - \epsilon_g$ for large distances between the nuclei. However, for large values of R, this quantity is exponentially small, so that the usual methods of the perturbation theory involving the expansion of ϵ_u and ϵ_g in powers of R^{-1} cannot be used. In an earlier paper[2], the present author proposed a method which makes it possible to determine asymptotically the exact value of $\epsilon_u - \epsilon_g$ for a system similar to the molecular hydrogen ion. Such a method is used in the present work to establish a relationship between the asymptotic form of $\epsilon_u - \epsilon_g$ and the asymptote to the radial atomic wave function.

Thus, knowing the properties of the atom, it is possible to determine the resonance charge-exchange cross section for the case when the value of this cross section is considerably larger than the corresponding atomic cross section. Since the assumption of a large value of the cross section is satisfied in all real cases of one-electron resonance charge exchange of ions and atoms, the proposed method makes it possible to calculate the resonance charge-exchange cross section without assuming any models.

2. For large distances between the nuclei

$$\varepsilon_u-\varepsilon_g=\oint_S(\psi_g\nabla\psi_u-\psi_u\nabla\psi_g)\,ds, \tag{2}$$

where ψ_g and ψ_u are the wave functions of the even and odd states of the quasimolecule, and S is a symmetry plane. Since, at large distances between the nuclei, ϵ_u and ϵ_g are equal within exponential accuracy, the corresponding eigenfunctions are described by identical equations

$$[-{}^1\!/_2\Delta+U(\mathbf{r}_1)+U(\mathbf{r}_2)]\psi_{u,g}=\varepsilon\psi_{u,g}. \tag{3}$$

Here, $\mathbf{r}_{1,2}$ is the distance from an electron to the corresponding ion; U is the potential of the electron-ion interaction, so that $U(r) \to -Z/r$, where Z is the ion charge; $|\epsilon|$ is the binding energy of the electron in the atom. It follows from Eq. (3) that, with exponential accuracy

$$\psi_{g,u}=2^{-1/2}[\psi(\mathbf{r}_1)\pm\psi(\mathbf{r}_2)], \tag{4}$$

where $\psi(\mathbf{r}_1)$, $\psi(\mathbf{r}_2)$ also satisfy Eq. (3). The function $\psi(\mathbf{r}_1)$ decays exponentially when the electron moves away from the first nucleus; the function $\psi(\mathbf{r}_2)$ behaves in the same way for the second nucleus. On reflection of the electron by the symmetry plane, $\psi(\mathbf{r}_1)$ becomes $\psi(\mathbf{r}_2)$ and $\psi(\mathbf{r}_2)$ becomes $\psi(\mathbf{r}_1)$.

If $r_2 \gg r_1$, the potential is $U(\mathbf{r}_2) \approx -Z/R$, and Eq. (3) for the function $\psi(\mathbf{r}_1)$ becomes

$$(-{}^1\!/_2\Delta+U(\mathbf{r}_1)-Z/R)\psi=\varepsilon\psi. \tag{5}$$

This is identical with the equation for the wave function of an atomic electron when the atom is in a constant field $-Z/R$. We shall assume that the atomic field $U(\mathbf{r})$ is spherically symmetrical so that the variables in Eq. (5) can be separated:

$$\psi(\mathbf{r}_1)=\chi(r_1)P_l^m(\cos\theta_1)e^{\pm im\varphi},$$

where r_1, θ_1, φ are the spherical coordinates near the first nucleus and $m > 0$. Such a separation of the variables in Eq. (3) is possible also for the function $\psi(\mathbf{r}_1)$ close to the axis which joins the two nuclei:

$$(r_1 / r_2) \sin \alpha_1 \ll 1, \tag{6}$$

where α_1 is the angle between $\mathbf{r}_1$ and $\mathbf{R}$. In this region between the nuclei, $r_2 \approx R - r_1$ and the interaction potential $U(r_1) = -Z/(R - r_1)$ is independent of the angle.

We shall assume that the integral in Eq. (2) converges near the axis at distances at which Eq. (6) is satisfied and the angular function is not yet affected. This is true provided

$$\gamma R \gg l^2, \tag{7}$$

where $\gamma = \sqrt{-2\epsilon}$, $|\epsilon|$ is the binding energy of the electron in the atom. With this assumption, averaging the values of the angular function $P_l^m(\cos\theta)$ along the axis, we obtain

$$\varepsilon_u - \varepsilon_g = \int_0^{2\pi} \frac{1}{2\pi} e^{im\varphi} e^{-im\varphi} d\varphi \int_0^{\pi} [P_l^m(\cos\theta)]^2 \sin\theta \frac{d\theta}{\pi} \int_0^{\infty} \rho \, d\rho$$
$$\times \chi\left(\sqrt{\left(\frac{R}{2} + z\right)^2 + \rho^2}\right) \frac{\partial}{\partial z} \chi\left(\sqrt{\left(\frac{R}{2} - z\right)^2 + \rho^2}\right)\Bigg|_{z=0},$$

where ρ, φ, z are the cylindrical coordinates in which the z-axis is directed along the axis of the quasimolecule and the origin is at the midpoint of the axis. Using the relationship

$$\partial\chi / \partial z|_{z=0} = R \partial\chi / \partial\rho^2|_{z=0},$$

we obtain

$$\varepsilon_u - \varepsilon_g = \frac{R}{4} \chi^2 \left(\frac{R}{2}\right). \tag{8}$$

This result was obtained by Firsov for the s-state.[1]

3. It follows from Eq. (3) that when the condition (6) is satisfied, i.e., $r_2 \approx R - r_1$, the radial wave function $\chi(r_1)$ satisfies the equation

$$-\frac{1}{2r_1} \frac{\partial^2}{\partial r_1^2}(r_1\chi) + U(r_1)\chi - \frac{Z}{R - r_1}\chi + \frac{l(l+1)}{r_1^2}\chi = -\frac{\gamma^2}{2}\chi.$$

At high values of r_1 $[U(r_1) = -Z/r_1]$, this equation has the quasiclassical solution $r_1\chi = e^{\Phi}$;

$$\Phi' = \left[\gamma^2 + \frac{2Z}{r_1} + \frac{2Z}{R - r_1} - \frac{l(l+1)}{r_1^2}\right]^{1/2}$$
$$\approx \gamma + \frac{Z}{r_1\gamma} + \frac{Z}{(R - r_1)\gamma} - \frac{l(l+1)}{2\gamma r_1^2};$$
$$r_1\chi = Ce^{-r_1\gamma}\left(\frac{r_1}{R - r_1}\right)^{Z/\gamma}, \quad \gamma r_1 \gg l(l+1), \ \frac{1}{\gamma}.$$

If $r_1 \ll R$ the above equation transforms into an equation for the radial wave function of an electron whose ionization potential is $\gamma^2/2 + Z/R$:

$$r_1\chi = Ce^{-r_1\gamma}(r_1/R)^{Z/\gamma}.$$

The asymptotic form of the wave function of the electron in the atom is then obtained by replacing the binding energy $\gamma^2/2 + Z/R$ with $\gamma^2/2$:

$$r_1\chi_{\text{at}}(r_1) = C \exp\{-r_1\sqrt{\gamma^2 - 2Z/R}\} \left(\frac{r_1}{R}\right)^{Z/\sqrt{\gamma^2 - 2Z/R}}$$
$$\approx C \exp\{-r_1\gamma - r_1 Z/R\gamma\} \left(\frac{r_1}{R}\right)^{Z/\gamma}. \tag{9}$$

Comparing the derived expressions, we shall relate the function $\chi(r)$ with the asymptote of the atomic wave function $\chi_{\text{at}}(r)$:

$$\chi(r_1) = \chi_{\text{at}}(r_1) \exp\{-r_1 Z/R\gamma\} \left(\frac{R}{R - r_1}\right)^{Z/\gamma}.$$

Using this relationship, we obtain for the asymptotic form of the difference given by Eq. (8):

$$\varepsilon_u - \varepsilon_g = \left(\frac{4}{e}\right)^{Z/\gamma} \frac{R}{4} \chi^2_{\text{at}}\left(\frac{R}{2}\right). \tag{10}$$

For a system consisting of a proton and a hydrogen atom $[\chi_{\text{at}}(r) = 2e^{-r}]$ this gives the well-known result[2-4]

$$\varepsilon_u - \varepsilon_g = 4Re^{-R-1}.$$

We shall now find the criterion of the applicability of the relationship (10). It is valid if [in addition to condition (7)] the radial wave function of the atom $\chi_{\text{at}}(r_1)$ is identical with its asymptotic value for $r_1 \lesssim R/2$. Then, near the middle of the axis joining the nuclei, the quasiclassical solution of the equation for χ, which may be related to the asymptote of the atomic wave function, is correct. The relationship (10) is valid provided $(\Phi^{(2)} \ll 1)$

$$R\gamma^2 / 2 \gg Z, \qquad R\gamma \gg 2l(l+1). \tag{11}$$

4. We shall now calculate the resonance charge-exchange cross section assuming that this value is much greater than the characteristic parameters of an atom. For $\gamma R_0 \gg 1/v$:

$$\int_{R_0}^{\infty} \frac{(\varepsilon_u - \varepsilon_g) R dR}{\sqrt{R^2 - R_0^2}} = \left(\frac{\pi R_0}{2\gamma}\right)^{1/2} [\varepsilon_u(R_0) - \varepsilon_g(R_0)],$$

so that the resonance charge-exchange cross section of Eq. (1), is $\sigma = \pi R_0^2/2$, where R_0 is given by the relationship

$$R_0^{1/2}[\varepsilon_u(R_0) - \varepsilon_g(R_0)] = 0.22\, v\gamma^{1/2}.$$

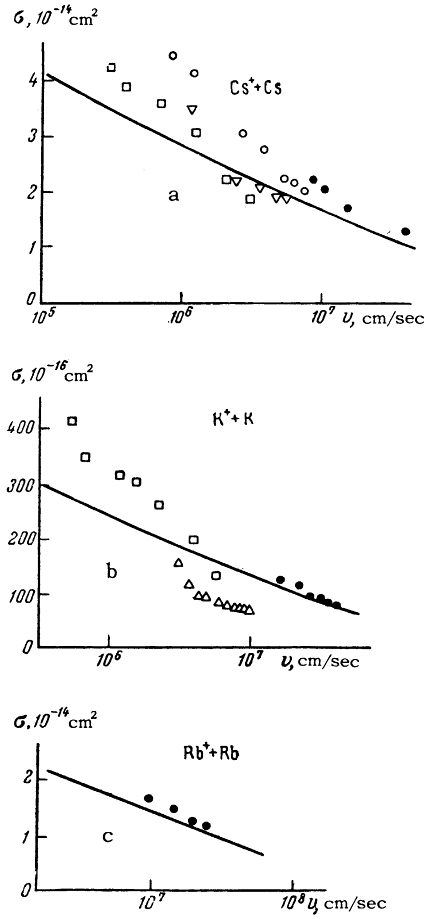
The asymptotic form of the atomic wave function is given by the expression (9):

$$\chi(r) = Ar^{Z/\gamma - 1}e^{-r\gamma}. \tag{12}$$

Using the expressions obtained here, we can establish a relationship between the resonance charge-exchange cross section $\sigma = \pi R_0^2/2$ and the relative collision velocity of the nuclei v:

$$R_0^{2Z/\gamma-1/2}e^{-R_0\gamma} = 0.22\frac{v}{A^2}\gamma^{1/2}e^{Z/\gamma},$$
$$R_0\gamma^2/2 \gg 1,\ R_0\gamma \gg 2l\,(l+1). \qquad (13)$$

5. The problem of determining the resonance charge-exchange cross section for an ion and its parent atom in slow collisions reduces to finding the coefficient A, whose magnitude is governed by the properties of the atom. The most accurate method of determining the constant A is based on the joining of the wave function obtained by the Hartree-Fock method with the wave function (12) at the boundary of the atom. The Hartree-Fock method gives sufficiently accurately the self-consistent field potential of the atomic core U(r) and the one-electron wave function $\chi(r)$ in the main part of the electron distribution. Therefore, if we expand this function as a system of one-electron eigenfunctions of the Hamiltonian in the self-consistent field approximation, $\chi = \Sigma_k c_k \chi_k$, then it is found that $1 - c_0^2 = \Sigma_{k\neq 0} c_k^2 \ll 1$. However, since the ground-state wave function χ_0 decays more rapidly than the wave functions of the excited states χ_k, the wave function χ far from the atom is determined by an admixture of excited states and does not give the asymptotically correct value.



Continuous curve was calculated theoreticaly using Eq. (16); □ – [5]; △ – [6]; ● – [7, 8]; ○ – [9].

The asymptotic behavior of the ground-state wave function χ_0 is given by Eq. (9) to within a constant factor. We shall use the fact that there is a range of distances from the nucleus where $(|\chi|^2 - |\chi_0|^2)/|\chi_0|^2 \ll 1$ still, but χ_0 is the asymptotic value of Eq. (12). We find the value of A by joining in this region of space the wave function χ, obtained by the Hartree-Fock method, and the asymptotic value of the wave function of Eq. (12) for an electron far from the nucleus but in the Coulomb field of the atomic core.

6. In the case of excited atoms and alkali metal atoms, the quantity A can be found sufficiently accurately using the fact that the electrons are distributed mainly in the region of the Coulomb interaction with the atomic core. In this region, the electron wave function is described by the equation (Z = 1)

$$\frac{1}{r}\frac{d^2(r\chi)}{dr^2} + \frac{2}{r}\chi - \frac{l(l+1)}{r^2}\chi - \gamma^2\chi = 0. \qquad (14)$$

We shall now impose on the radial wave function of the electron χ a boundary condition at $r \to 0$ which gives the correct electron binding energy. Having found the solution of Eq. (14) with the corresponding boundary condition, which decreases at $r \to \infty$, and having normalized the resultant wave function, we can determine the coefficient A.

In the case of integral values $\gamma^{-1} \geq l + 1$, Eq. (14) is identical with the equation for the wave function of an electron in an excited hydrogen atom. Then

$$A(\gamma) = A_0(\gamma)$$
$$\equiv 2^{1/\gamma}\gamma^{1/\gamma+1}\Gamma^{-1/2}(\gamma^{-1} - l)\,\Gamma^{-1/2}(\gamma^{-1} + l + 1). \qquad (15)$$

For nonintegral values of γ^{-1}, we cannot normalize the wave function which is the solution of Eq. (14). However, since the normalization factor, and consequently also $A(\gamma)$ [like $A_0(\gamma)$], are monotonic functions of γ^{-1} and for integral values of γ^{-1} the values of $A(\gamma)$ and $A_0(\gamma)$ are identical, we can expect that for nonintegral values of γ^{-1} the coefficient $A(\gamma)$ does not differ greatly from $A_0(\gamma)$. Using such an interpolation, we obtain on the basis of Eq. (13) a dependence of the resonance charge-exchange cross section $\sigma = \pi R_0^2/2$ on the relative velocity of the colliding nuclei v (Z = 1):

$$\frac{(4/e)^{1/\gamma}\gamma^2(R_0\gamma)^{2/\gamma-1/2}e^{-R_0\gamma}}{\Gamma(\gamma^{-1} - l)\,\Gamma(\gamma^{-1} + l + 1)} = 0.22v. \qquad (16)$$

The result obtained is applicable to the case of resonance charge-exchange in excited atoms and in alkali-metal atoms. A comparison of the dependence of the resonance charge-exchange cross section on the velocity given by Eq. (16) with the experimental data for alkali metals[5-9] is presented in the figure.

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