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Abstract

Full Text

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RESONANT TRANSFER OF EXCITATION IN COLLISIONS OF HEAVY ATOMS

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1. The process of excitation transfer plays a major role in the physics of weakly ionized gases. Especially important is the process of resonant excitation transfer that occurs in the collision of two identical atoms, one of which is in the ground state, while the other is excited in such a way that an optical dipole transition to the ground state is allowed for it. This process is resonant in two respects. First, the transfer of excitation occurs without a change in the energy of the electrons. Second, the interaction in this case is the largest, dipole-dipole:

$$V = \mathbf{r}_1 \mathbf{r}_2 / R^3 - 3(\mathbf{r}_1 \mathbf{R})(\mathbf{r}_2 \mathbf{R}) / R^5, \tag{1}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the radius vectors of the electrons relative to the nuclei of their atoms (we neglect electron exchange), and $\mathbf{R}$ is the vector of the relative position of the atomic nuclei. The atomic system of units is used.

Previously ([1,2]), the case of S- and P-states of electrons in atoms was considered, with the fine splitting of the P-state neglected. In the present work the same problem is considered in the opposite case. The paper also calculates the cross section for the change of the hyperfine state of the ground S-state as a result of excitation transfer, calculated earlier ([3]) for the case of small fine splitting.

2. Let us calculate the cross section for exchange between the states $S_{1/2,m}$ and $P_{j,m'}$ in a collision of identical one-electron atoms ($j = {}^3/2$ and ${}^1/2$). At small relative velocities v, the internuclear distances are large compared with atomic dimensions, so that the wave functions of the electron system are products of atomic functions with specified principal quantum numbers. For a given j—the total angular momentum of the excited P-state—these products differ only in the values of the projections of the angular momenta m and m'. We shall regard the nuclei as moving along rectilinear classical trajectories. We direct the quantization axis z along the relative angular momentum of the nuclei, and relate the axes x and y to $\mathbf{v}$ and ρ.

The large magnitude of the fine splitting permits, at small v, the excitation transitions $P_{1/2,m'}$ and $P_{3/2,m'}$ to be considered independently of one another, so that we obtain two cross sections $\sigma^{1/2}$ and $\sigma^{3/2}$ for $j = {}^1/2$ and $j = {}^3/2$, respectively.

We shall assume that the Hamiltonian of the system consists of the sum of the atomic Hamiltonians, in which the spin-orbit interaction is included, and the interaction (1). We neglect the fine interaction of the electrons with one another, since it has an additional smallness $e^{-\alpha R}$ due to the weak overlap of the electron wave functions. For identical atoms, the Hamiltonian of the complete system is symmetric with respect to interchange of the states. We therefore form from the atomic functions their combinations, which will be eigenfunctions of the state-interchange operator:

$$\Psi^{\pm}_{m,m'} = \frac{1}{\sqrt{2}}\left[\Phi_{1/2,m}(\mathbf{r}_1)\Phi_{j,m'}(\mathbf{r}_2) \pm \Phi_{1/2,m}(\mathbf{r}_2)\Phi_{j,m'}(\mathbf{r}_1)\right], \tag{2}$$

where $\Phi_{1/2,m}$ is the wave function of the S-state, and $\Phi_{j,m'}$ is that of the P-state.

The complete Hamiltonian is also symmetric with respect to reflection in the plane $z = 0$. As a result of this symmetry, the system of Schrödinger equations for the expansion coefficients $a^{\pm}_{m,m'}$ of the total function in the functions (2) splits into two independent halves. Let us introduce, instead of the time t, a new variable $\xi = vt/R$ $(-1 \le \xi \le +1)$; then we obtain the systems:

$$\pm i\,\frac{d}{d\xi}\begin{pmatrix} a^{\pm}_{\frac{1}{2},\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},-\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},\frac{1}{2}} \\ a^{\pm}_{\frac{1}{2},-\frac{1}{2}} \end{pmatrix} = q\begin{pmatrix} -\frac{3}{2} & 0 & 0 & -\frac{3\sqrt{3}}{2}f(\xi) \\ 0 & -\frac{3}{2} & -\frac{3\sqrt{3}}{2}f^*(\xi) & 0 \\ 0 & -\frac{3\sqrt{3}}{2}f(\xi) & -\frac{1}{2} & 2 \\ -\frac{3\sqrt{3}}{2}f^*(\xi) & 0 & 2 & -\frac{1}{2} \end{pmatrix} \times \begin{pmatrix} a^{\pm}_{\frac{1}{2},\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},-\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},\frac{1}{2}} \\ a^{\pm}_{\frac{1}{2},-\frac{1}{2}} \end{pmatrix}; \tag{3}$$

$$\pm i\,\frac{d}{d\xi}\begin{pmatrix} a^{\pm}_{\frac{1}{2},\frac{1}{2}} \\ a^{\pm}_{\frac{1}{2},-\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},-\frac{1}{2}} \end{pmatrix} = q\begin{pmatrix} 2 & 0 & -\frac{\sqrt{3}}{2} & -\frac{3}{2}f(\xi) \\ 0 & 0 & -\frac{9}{2}f^*(\xi) & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{9}{2}f(\xi) & 0 & 0 \\ -\frac{3}{2}f^*(\xi) & -\frac{\sqrt{3}}{2} & 0 & 2 \end{pmatrix}\begin{pmatrix} a^{\pm}_{\frac{1}{2},\frac{1}{2}} \\ a^{\pm}_{\frac{1}{2},-\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},\frac{3}{2}} \\ a^{\pm}_{-\frac{1}{2},-\frac{1}{2}} \end{pmatrix}; \tag{3'}$$

for $j = 3/2$, and for $j = 1/2$:

$$\pm i\,\frac{d}{d\xi}\begin{pmatrix} a^{\pm}_{\frac{1}{2},\frac{1}{2}} \\ a^{\pm}_{-\frac{1}{2},-\frac{1}{2}} \end{pmatrix} = q\begin{pmatrix} 1 & -3f(\xi) \\ -3f^*(\xi) & 1 \end{pmatrix}\begin{pmatrix} a^{\pm}_{\frac{1}{2},\frac{1}{2}} \\ a^{\pm}_{-\frac{1}{2},-\frac{1}{2}} \end{pmatrix}; \qquad q \equiv \frac{1}{6}\frac{|\langle d\rangle|^2}{\rho^2 v}; \tag{4}$$

$$\pm i\,\frac{d}{d\xi}\begin{pmatrix} a^{\pm}_{\frac{1}{2},-\frac{1}{2}} \\ a^{\pm}_{-\frac{1}{2},\frac{1}{2}} \end{pmatrix} = q\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} a^{\pm}_{\frac{1}{2},-\frac{1}{2}} \\ a^{\pm}_{-\frac{1}{2},\frac{1}{2}} \end{pmatrix}; \qquad f(\xi) = 2\xi^2 - 1 - 2i\xi\sqrt{1-\xi^2}.$$

Here $\langle d \rangle$ is the dipole moment of the optical transition.

If the population of the sublevels with different m and m' is uniform and at $\xi = -1$ $(t = -\infty)$ the excitation is on atom 2, then the initial condition is:

$$\Psi(t=-\infty) = \frac{1}{4} \sum_{m,m'} \left(\Psi^{+}_{m,m'} + \Psi^{-}_{m,m'} \right), \qquad j = 3/2;$$

$$\Psi(t=-\infty) = \frac{1}{2\sqrt{2}} \sum_{m,m'} \left(\Psi^{+}_{m,m'} + \Psi^{-}_{m,m'} \right), \qquad j = 1/2; \qquad \int |\Psi|^2 \, dV_1 \, dV_2 = 1. \tag{5}$$

The summation here is carried out over all possible values $m = 1/2, -1/2$ and m' (3/2, 1/2, $-1/2$, $-3/2$ for $j = 3/2$, and 1/2, $-1/2$ for $j = 1/2$). For these initial values of $a^{\pm}_{m,m'}$, the probabilities of excitation transfer are

$$W_{3/2}(q) = \frac{1}{16} \left| \sum_{m,m'} \left(a^{+}_{m,m'}(\xi = 1) - a^{-}_{m,m'}(\xi = 1) \right) \right|^2, \qquad j = \frac{3}{2};$$

$$W_{1/2}(q) = \frac{1}{8} \left| \sum_{m,m'} \left(a^{+}_{m,m'}(\xi = 1) - a^{-}_{m,m'}(\xi = 1) \right) \right|^2, \qquad j = \frac{1}{2}. \tag{6}$$

To calculate the probability of a change in the spin projection for the S-state, the initial conditions must be

$$\Psi(t=-\infty) = \frac{1}{2\sqrt{2}} \sum_{m=1/2,\, m'} \left(\Psi^{+}_{1/2,m} + \Psi^{-}_{1/2,m'} \right), \qquad j = \frac{3}{2};$$

$$\Psi(t=-\infty) = \frac{1}{2} \sum_{m=1/2,\, m'} \left(\Psi^{+}_{1/2,m'} + \Psi^{-}_{1/2,m'} \right), \qquad j = \frac{1}{2}. \tag{5'}$$

Here the summation is extended over all m', and $m = 1/2$.

Fig. 1. a–probability of excitation transfer: 1–$W_{1/2}(q)/q^2$; 2–$W_{3/2}(q)^2$; b–probability of a change in the electron spin in the S-state with and without excitation transfer; the constants α and β in Table 1 were determined by integration up to $q = 2$; 1–$\omega^{(1)}_{1/2}(q)/q^2$; 2–$\omega^{(1)}_{3/2}(q)/q^2$; 3–$\omega^{(0)}_{1/2}(q)/q^2$; 4–$(\omega^{(0)}_{3/2}(q)/q^2) \cdot 10$.

The probabilities of a change of this projection to $m = -1/2$ under condition $(5')$ are

$$\omega^{(0)}_{3/2} = \frac{1}{8}\left| \sum_{m=-1/2,\, m'} \left(a^{+}_{-1/2,m'}(+1) + a^{-}_{-1/2,m'}(+1) \right) \right|^2 ;$$

$$\omega^{(1)}_{3/2} = \frac{1}{8}\left| \sum_{m=-1/2,\, m'} \left(a^{+}_{-1/2,m'}(+1) - a^{-}_{-1/2,m'}(+1) \right) \right|^2 , \qquad j = \frac{3}{2};$$

$$\omega^{(0)}_{1/2} = \frac{1}{4}\left| \sum_{m=-1/2,\, m'} \left(a^{+}_{-1/2,m'}(+1) + a^{-}_{-1/2,m'}(+1) \right) \right|^2 ;$$

$$\omega^{(1)}_{1/2} = \frac{1}{4}\left| \sum_{m=-1/2,\, m'} \left(a^{+}_{-1/2,m'}(+1) - a^{-}_{-1/2,m'}(+1) \right) \right| ; \qquad (6')$$

$$\omega_{3/2} = \omega^{(0)}_{3/2} + \omega^{(1)}_{3/2} = \frac{1}{4}\left[\left| \sum_{m=-1/2,\ m'} a^{+}_{-1/2,m'} \right|^2 + \left| \sum_{m=-1/2,\ m'} a^{-}_{-1/2,m'} \right|^2 \right] ;$$

$$\omega_{1/2} = \omega^{(0)}_{1/2} + \omega^{(1)}_{1/2} = \frac{1}{2}\left[\left| \sum_{m=-1/2,\ m'} a^{+}_{-1/2,m'} \right|^2 + \left| \sum_{m=-1/2,\ m'} a^{-}_{-1/2,m'} \right|^2 \right] .$$

Here the summation is carried out over all m' and $m = -1/2$, the superscript (0) denoting probabilities without transfer of excitation, and (1) with transfer of excitation, so that $\omega^{(0)}_{3/2}$ is the probability of changing the spin projection in an S-state to the opposite one, under the condition that the $P_{3/2}$ excitation remains on its atom.

The cross sections for excitation transfer are

$$\sigma_{3/2} = \alpha_{3/2}\sigma_0; \qquad \sigma_{1/2} = \alpha_{1/2}\sigma_0; \qquad \sigma_0 = \frac{|\langle d \rangle|^2}{v}; \qquad \alpha_{3/2,1/2} = \frac{\pi}{6}\int_0^\infty \frac{W_{3/2,1/2}(q)}{q^2}\, dq, \qquad (7)$$

and the cross sections for changing the spin projection of the S-electron are

$$Q^{(0),(1)}_{3/2,1/2} = \beta^{(0),(1)}_{3/2,1/2}\sigma_0; \qquad Q_{3/2,1/2} = \left(\beta^{(0)}_{3/2,1/2} + \beta^{(1)}_{3/2,1/2} \right)\sigma_0; \qquad \beta^{(0),(1)}_{3/2,1/2} = \int_0^\infty \frac{\omega^{(0),(1)}_{3/2,1/2}(q)}{q^2}\, dq. \qquad (8)$$

The solution of the second system (4) can be written down at once:

$$a^{\pm}_{1/2,-1/2} = A + Be^{\pm 2iq\xi}, \qquad a^{\pm}_{-1/2,1/2} = A - Be^{\pm 2iq\xi}, \tag{9}$$

where A and B are constants of integration.

Table 1

j	α	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(0)} + \beta^{(1)}$
3/2	0.57	0.05	0.21	0.26
1/2	1.65	0.42	0.68	1.10

The remaining systems were solved numerically on a computer. The volume of computation is noticeably reduced if one uses the properties of the solutions of systems (3), (3′), and (4): $a^{\pm}_{m,m'} = (a^{\pm}_{-m,-m'})^*$.

3. The cross section Q_{st} for changing the hyperfine state of the S-electron is related to the cross section for changing the projection of its spin (8) by the relation

$$Q_{\text{st}}(I + 1/2 \to I - 1/2) = \frac{2I+1}{4(I+1)}Q; \qquad Q_{\text{st}}(I - 1/2 \to I + 1/2) = \frac{2I+1}{4}Q, \tag{10}$$

where I is the spin of the nucleus of the atom on which the S-electron is located.

4. Table 1 gives the calculated values of α and β; Table 2 gives the dipole moments of the resonance transitions of alkali atoms, found from the known oscillator strengths[4], and the magnitudes of the fine splitting Ω of the first excited state of these atoms, in atomic units.

All calculated probabilities are shown in Fig. 1.

Table 2

	Cs	Rb	K	Na	Li
$\lvert\langle d\rangle\rvert^2$	14.1	13.0	12.5	9.5	5.65
Ω	$2.52 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$	$2.63 \cdot 10^{-4}$	$7.82 \cdot 10^{-5}$	$1.55 \cdot 10^{-6}$

5. From the very beginning it was assumed that the splitting Ω of the $P_{1/2} - P_{3/2}$ levels is large in comparison with (1). As is seen from the results, for this it is necessary (since the cross section $\sim 1/v$) that

$$v \ll \Omega^{2/3}.$$

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Note: Figure translations are in progress. See original paper for figures.