PHYSICAL REVIEW A VOLUME 52, NUMBER 3 SEPTEMBER 1995

Classical theory of l-changing transitions in collisions between Rydberg atoms and ions

A. K. Kazansky and V. N. Ostrovsky
Institute of Physics, The University of St. Petersburg, 198904 St. Petersburg, Russia
(Received 30 March 1995)

The l-changing transitions in collisions of Rydberg atoms with ions, $A(nl_0)+B^+ \rightarrow A(nl)+B^+$, are considered within the classical approximation for atomic electron motion. The elliptic orbit of the electron evolves slowly under the influence of the time-dependent electric field exerted by the incident ion. The quantum electron state is represented by an ensemble of classical trajectories. Within the dipole approximation extremely simple analytical formulas for the final-state l-distribution function are obtained for a fixed value of the impact parameter. The influence of the non-Coulomb core is taken into account approximately. The results of our calculations compare favorably with recent experimental data for the $Na^+(26d, 28d)$ Rydberg atom. The method can be extended to the calculation of distributions over various observables other than l.

PACS number(s): 34.50.Pi, 34.60.+z, 34.10.+x

A large variety of inelastic transitions occur in collisions of Rydberg atoms (nl_0) with ions. The l-changing transitions $nl_0 \rightarrow nl$ possess the largest cross sections. The current state of the theory and the experiment was reviewed in a recent paper by Sun and MacAdam [1].

All the theoretical studies have used the dipole approximation for the ion–Rydberg-atom interaction. For the higher collision velocities the direct dipole transitions $\Delta l = \pm 1$ dominate. As v decreases, the processes with larger $|\Delta l|$ become more and more significant. For their description some sort of coupled-channel treatment is required. While the reduced collision velocity vn is not large, it is natural to include in the calculations only the atomic states with the same principal quantum number n as that in the initial Rydberg state. However, the number of such states ($\sim n^2$) is prohibitively large for the numerical calculations ($n^2 = 784$ for $n = 28$), especially bearing in mind that the transitions are induced by very-long-range interactions. To tackle the task, Beigman and Syrkin [2] used a special *ad hoc* procedure to reduce the number of coupled equations to n.

We develop an alternative approach based on the analysis of the slow evolution of the classical trajectory of the Rydberg electron caused by the time-dependent force exerted by the moving incident ion. Such a theory is expected to be reasonable if the relative collision velocity vn is not too high.

Within the dipole approximation for the interaction, the Rydberg atom is affected by the uniform electric field $\vec{E}(t)$. In the frame that rotates with the internuclear axis, the direction of electric field is fixed, but an additional Coriolis force emerges. It is equivalent to an effective magnetic (Larmor) field $\vec{H}(t)$ that is *perpendicular* to the collision plane. The strengths of both fields have the same time dependence [$E(t) = ZR(t)^{-2}$, $H = bvR(t)^{-2}$, where $\vec{R}(t)$ is the internuclear vector, b is the impact parameter, Z is the incident ion charge]. The problem can be solved explicitly both classically and quantum mechanically for the case of the hydrogen atom.

The classical problem (with time-independent fields having arbitrary directions) was considered by Epstein [3] and Pauli [4] (more precisely, these authors treated the problem with the old quantum mechanics method which implied analysis of the slow evolution of classical trajectories). The electron orbit was characterized by the orbital momentum $\vec{l}$ and the Runge-Lenz vector $\vec{A}$ directed from the atomic nucleus towards the orbit aphelion. The slow evolution of trajectories can be described as the uniform precession of the vectors $\vec{J}_1 = \frac{1}{2}(\vec{l}+\vec{A})$ and $\vec{J}_2 = \frac{1}{2}(\vec{l}-\vec{A})$. The axes of precession are directed along the vectors $\vec{\omega}_1 = \frac{3}{2}n\vec{E}+\vec{H}$ and $\vec{\omega}_2 = \frac{3}{2}n\vec{E}-\vec{H}$, respectively. The precession frequencies are equal to ω_1 and ω_2.

Although in the collision problem the electric and magnetic field strengths are nonstationary, they have the same (up to the constant factors) time dependence. As a result, the precession is uniform in the *effective* time, which is the angle Φ of rotation of the internuclear vector $\vec{R}(t)$:

$$\Phi(t) = \int_{-\infty}^{t} \frac{L}{\mu R^2(t')}\, dt' \tag{1}$$

(μ is the reduced mass of the colliding particles, $L = \mu bv$). The frequencies of the precession in the Φ variable coincide,

$$\omega_1 = \omega_2 = \omega_\Phi = \sqrt{1+\left(\frac{3Zn\mu}{2L}\right)^2}. \tag{2}$$

The quantum treatment for the excited hydrogen atom in crossed electric and magnetic fields was presented by Demkov *et al.* [5]. The general solution of the l-changing collision problem for the *quantum electron* was given by Demkov *et al.* [6], Ostrovsky and Solovyov [7], and Ostrovsky [8], respectively, for *classical, semiclassical, and quantum descriptions of the motion of atomic nuclei.* This solution is expressed via finite sums containing Wigner functions and Clebsch-Gordan coefficients, although it does not provide a clear idea of the process. We treat the *electron motion* within the framework of *classical mechanics.* According to the correspondence principle, the results obtained are to be related directly to the classical limit of the quantum solution.

Note that this development is rigorous only in the case of the hydrogen atom (or hydrogenlike ion) with the energy

levels degenerate in the orbital quantum number l. Its application to the Rydberg atoms with non-Coulomb core needs some additional analysis (see below).

We represent the quantum electron state by an ensemble of classical trajectories. Below we consider the Rydberg atom being initially in an s state. In this case ($l_0=0$) the elliptical classical electron orbit is squeezed into the interval of line that is directed along the vector $\vec{A}_0$. The initial quantum s state is represented by an ensemble of such trajectories, randomly oriented in space. The geometrical picture of uniform precession leads to explicit algebraic expressions for the final values of $\vec{l}$ and $\vec{A}$ via the initial values $\vec{l}_0$ and $\vec{A}_0$.

We choose the spherical coordinate system with the axis directed along the effective magnetic field, i.e., perpendicular to the collision plane. Then the initial (i.e., prior to the collision) orientation of the classical (i.e., of the vector $\vec{A}_0$) ($l_0=0$) orbit is specified by the spherical angles ϑ, φ. The geometrical calculations outlined above provide the following expression for the final (postcollision) value of the electron orbital momentum:

$$\frac{l}{n}=G(\vartheta,\varphi), \quad [G(\vartheta,\varphi)]^2=\epsilon_m^2[1-\sin^2\vartheta\cos^2(\varphi+\zeta)], \tag{3}$$

where

$$\epsilon_m=2\sin\gamma\,|\sin(\Omega/2)|\,\sqrt{\cos^2\gamma\,\sin^2(\Omega/2)+\cos^2(\Omega/2)}\,, \tag{4}$$

$$\Omega=\frac{\Delta\Phi}{\cos\gamma}, \quad \tan\gamma=\sqrt{\omega_\Phi^2-1}=\frac{3nZ}{2bv}, \quad \tan\zeta=\frac{\cot(\Omega/2)}{\cos\gamma}. \tag{5}$$

Here Ω is just the angle of precession described above; $\Delta\Phi$ is the angle of internuclear axis rotation in the course of the collision ($\Delta\Phi=\pi$ for the rectilinear trajectory).

For each value of the impact parameter b, the formulas (3) map the initial ensemble of the classical trajectories on the final values of the reduced orbital momentum $\epsilon=l/n$. Averaging over the ensemble (i.e., integration over ϑ, φ) results in the l distribution generated by the collision with given b. The distribution function over the reduced orbital momentum is defined as follows:

$$f(\epsilon;\,b,v)=\frac{1}{4\pi}\int_0^\pi \sin\vartheta\;d\vartheta\int_0^{2\pi}d\varphi\;\;\delta(\epsilon-G(\vartheta,\varphi)). \tag{6}$$

The total differential cross section of the orbital momentum transfer reads

$$\frac{d\sigma(\epsilon)}{d\epsilon}=2\pi\int f(\epsilon;\,b,v)\;\;b\;db, \tag{7}$$

which can be compared with the experiment.

The integration (6) can be carried out in a closed form:

$$f(\epsilon;\,b,v)=\frac{\epsilon}{\epsilon_m\sqrt{\epsilon_m^2-\epsilon^2}}\,(\epsilon<\epsilon_m), \quad f(\epsilon;\;\;b,v)=0\,(\epsilon>\epsilon_m). \tag{8}$$

This distribution has a remarkably simple analytical form with the single parameter $\epsilon_m(b,v)$, which means the electron maximal orbital momentum generated in the collision with given b and v. [Formula (8) is a generalization of the distribution function obtained by Kazansky [9] for the case of pure Stark effect.] The region $\epsilon>\epsilon_m$ is forbidden for the classical population. Note the weak (square root) singularity of the distribution functions for $\epsilon=\epsilon_m$. In the quantum calculations such singularities are typically replaced by Airy-type patterns. The singularities are to be smoothed out by the integration in Eq.(7) over b, which will simplify the quantum mechanical intricacies.

It is quite natural that only low values of l are generated in the remote and fast collisions ($\epsilon_m\sim 2\gamma$ for $\gamma\ll 1$). Perhaps, more unexpected is the fact that for close encounters the high-l generation is also suppressed classically for dynamic reasons. In geometrical terms this stems from the fact that when γ approaches $\frac{1}{2}\pi$, the precession angle Ω increases to infinity. Since the expression (4) contains only trigonometric functions of Ω, it behaves quasiperiodically as the reduced impact parameter $x=bv/n$ decreases. This leads to suppression of the large-l generation to the extent depending on the value of $\sin\Omega$.

The summation over impact parameter b in (7) needs some care. For small impact parameters the dipole approximation fails. The analysis of classical Rydberg electron trajectories beyond this approximation was given by Kazansky [10]. It suggests that the dipole approximation is applicable, provided the impact parameter appreciably exceeds the dimension of the electron orbit ($2n^2$). As a lower limit of the integration, we choose (somewhat arbitrarily) this value twice: $b_{min}=4n^2$. Our test calculations have demonstrated that the variation of b_{min} practically does not affect the results.

The integral (7) tends to infinity for $l\to 0$ due to the contribution of the large impact parameters b. Actually a finite effective upper limit for b exists because of the level splitting within the n manifold. For the hydrogen atom (and hydrogenlike ions) this is the fine structure splitting (cf. calculations by Chibisov [11] for $n=2$). For nonhydrogenic Rydberg atoms the splitting induced by the atomic core is much larger.

Our calculations below address the experiment [1] with Rydberg Na(nd) atoms. The s and p states of the sodium atom have large quantum defects. Therefore they are effectively excluded from the hydrogenlike n manifold where efficient l mixing occurs. The d levels have a small quantum defect [1]: $\delta_d=0.0135$. As an incident ion approaches the Rydberg atom, the Coulomb degenerate manifold of the states with $l\geqslant 3$ experiences the linear Stark effect, whereas the d level is only weakly (quadratically) perturbed by the ion field. Transitions from the d state to the higher l states become efficient when the *outermost* level in the Stark-split manifold [$\Delta E\approx 3Zn^2/(2R^2)$] crosses the d level. When the field strength further increases (i.e., the ion approaches the atom), the d state becomes strongly mixed with the bulk ($l\geqslant 3$) of the hydrogenlike manifold. This estimate gives the maximal value of the internuclear separation: $R_{max}=\sqrt{3n^5Z/2\delta_d}$ (below we assume that the charge of the incident ion is $Z=1$). The simplest way to introduce the

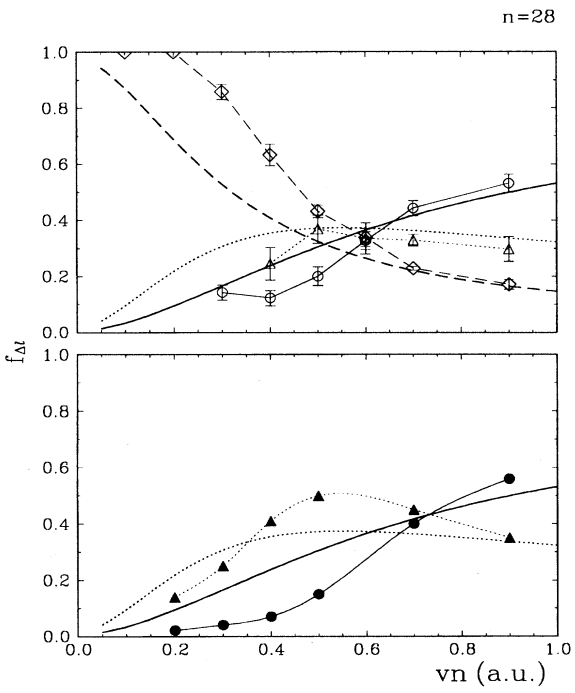

FIG. 1. Fractional populations for the l mixing in the excited sodium atom as a function of the reduced collision velocity vn for various values of the orbital momentum transfer Δl. Open symbols, experimental data by Sun and MacAdam [1]; closed symbols, quantum model by Beigman and Syrkin [2]. Circles, Na($28d$) $\rightarrow$Na($28f$) transition; solid curve, present theory for $\Delta l=1$; triangles, Na($28d$)$\rightarrow$Na($28g,h$) transitions; dotted curve, present theory, sum for $\Delta l=2$ and $\Delta l=3$; diamonds, Na($28d$)$\rightarrow$Na($28l$), $l\geq 6$; dashed curve, present theory, sum for $27\geq\Delta l\geq 4$.

core effect in the calculation is provided by choosing of the upper limit of integration (7) as $b_{max}=R_{max}$.

We have calculated first the integrated l distributions for the quasihydrogenic atom,

$$\sigma_I(l) = \int_0^{l/n} d\epsilon \frac{d\sigma(\epsilon)}{d\epsilon} = 2\pi\int_{b_{min}}^{b_{max}} b\, db \quad \epsilon_m \times\left(1-\sqrt{1-\frac{l^2}{\epsilon_m^2 n^2}}\right), \tag{9}$$

for various values of the reduced velocity vn. The distributions are shifted to higher values of l as vn decreases. For $vn\sim 1$ the dependence of $\sigma_I(l)$ on vn is quite weak.

The cross sections for the transition into *quantum* electron states with the integer orbital momentum l are obtained using the binning procedure. We employ the prescription of Becker and MacKellar [12], taking $\sigma(l)=\sigma_I(l+1)-\sigma_I(l)$. To compare the present model with the experimental data, we calculate the velocity dependence of the fractional population $f_l(v)$ of the given final l state ($l\neq l_0$). These quantities are introduced [1] as the ratios $f_l=\sigma(l)/\Sigma_{l'\neq l_0}\sigma(l')$ between the cross section $\sigma(l)$ of the transition to the state with the given l and the integral cross section $\Sigma_{l'\neq l_0}\sigma(l')$ for depopulation of the initial l_0 state (in the present case, $l_0=0$). Hence the sum over all fractional populations ($l\neq l_0$) is equal to 1.

The application of the present theory to the collisions of Na(nd)($n=28$) with the ion is based on the fact that the corresponding classical electron orbit has very high eccentricity (since $l_0=2\ll n$). It can be approximately replaced by the straight-line orbit for s states. As discussed above, s and p states of Na(nl) are effectively excluded from the l-mixing process. The distribution over l for the quasihydrogenic atom (with $l_0=0$) is presumed to be the same as the distribution over the orbital momentum transfer Δl in the sodium atom. Hence in Fig. 1 the experimental data [1] for the fractional population $f_{\Delta l}$ of f states [transition Na($28d$)$\rightarrow$Na($28f$), $\Delta l=1$] are compared with the present quasihydrogenic results for $l=1$; the population of Na g states ($\Delta l=2$) corresponds to our result for $l=2$, and so on.

The evolution (with vn) of the fractional populations for the lowest values of l is shown in Fig. 1, in comparison with recent experimental [1] and theoretical [2] results. Our theory agrees with experiment in the qualitative behavior of the distributions. For the lower l state the quantitative agreement is pretty good. For the fractional population of the states with $l\geq 6$ the differences are somewhat larger. The results represented in Fig. 2 demonstrate that the correspondence between the present theory and the experimental data is even better for $n=26$. The present calculations are very simple and applicable for low relative velocites vn where calculations by other methods are difficult.

The important point to be stressed is that our approach is the classical analog of the quantum close-coupling calculations within the given n manifold. Indeed, the present theory considers slow evolution of the classical electron trajectory, so that the electron principle quantum number (the classical

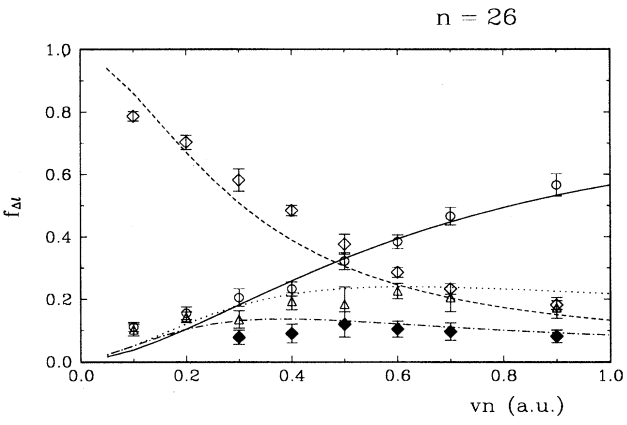

FIG. 2. The same as in Fig. 1, but for the $26d$ initial state of the sodium Rydberg atom. The symbols correspond to the experimental data of Sun and MacAdam [1]. Open circles, Na($26d$)$\rightarrow$Na($26f$) transition; solid curve, present theory for $\Delta l=1$; triangles, Na($26d$)$\rightarrow$Na($26g$) transition; dotted curve, present theory for $\Delta l=2$; closed diamonds, Na($26d$)$\rightarrow$Na($26h$) transition; dash-dotted curve, present theory for $\Delta l=3$; diamonds, Na($26d$) $\rightarrow$Na($26l$), $l\geq 6$; dashed curve, present theory, sum for $25\geq\Delta l\geq 4$.

adiabatic invariant) is conserved. This implies that the perturbation varies slowly with time. The confinement of the quantum close-coupling scheme to the fixed-n manifold actually has the same meaning, although the real calculations were carried out [2] and compared with experiment [1] for the relative collision velocities vn, which are not very small (the most significant experimental data were obtained in the interval $0.4 \leqslant vn \leqslant 0.9$). Introducing the cutoff internuclear distance R_{max} also has its analogy in the quantum calculations, where the energy splitting between Na d levels and the hydrogenlike ($l \geqslant 3$) manifold was introduced in the equations of close-coupling scheme, while the s and p states were omitted.

Moreover, in one respect the present theory seems to be superior to the version of the quantum close-coupling scheme used by Beigman and Syrkin [2]. Indeed, these authors had simplified drastically the exact quantum equations using an *ad hoc* procedure ("averaging of the close-coupling equations over the magnetic quantum number m").

The present scheme may be applied to the calculation of the distribution over various characteristics of the atom; for example, over the multipole moments of the electron cloud in the Rydberg atom generated by the collision, or over the parabolic quantum numbers (which can be used for the classification of the Na** states with $m > 3$). The classical approach may be generalized to the case $l_0 \neq 0$ and to the Rydberg atoms with initial orbital polarization.

The information on the distributions over m and parabolic quantum numbers (which cannot be obtained within the Beigman-Syrkin scheme [2]) seems to be extremely important for interpretation of the experimental observations. Actually in the current experiments [1,13] the identification of the final Rydberg states is based on the selective field ionization technique and some additional assumptions, such as a uniform distribution over m sublevels (for the given l). The present approach in principle is capable of providing the missing information, although additional work is necessary.

We also anticipate that the classical model may be useful as a constituent part of the description of the other collision processes with the Rydberg atoms (e.g., the charge exchange with the orbitally polarized atoms [13,14]).

This work was initiated during the stay of V.N.O. at the University of Bielefeld, which was supported by the Deutsche Forschungsgemeinschaft, Grant No. SFB 216. The work was continued during his visit to the University of Aarhus, Denmark. V.N.O. is thankful to both these institutions for support and hospitality. Fruitful discussions with H.O. Lutz, Z. Roller-Lutz, K. Taulbjerg, E. Horsdal-Pedersen, K.B. MacAdam, and B.D. DePaola are highly appreciated. A.K.K. is greatly indebted to Mark Syrkin for his hospitality.

[1] X. Sun and K. B. MacAdam, Phys. Rev. A **47**, 3913 (1993).

[2] I. L. Beigman and M. I. Syrkin, Zh. Eksp. Teor. Fiz. **89**, 400 (1985) [Sov.Phys. JETP **62**, 226 (1985)].

[3] P. S. Epstein, Phys. Rev. **22**, 202 (1923).

[4] W. Pauli, Z. Phys. **36**, 336 (1926).

[5] Yu. N. Demkov, B. S. Monozon, and V. N. Ostrovsky, Zh. Eksp. Teor. Fiz. **57**, 1431 (1969) [Sov. Phys. JETP **30**, 775 (1970)].

[6] Yu. N. Demkov, V. N. Ostrovsky, and E. A. Solovyov, Zh. Eksp. Teor. Fiz. **66**, 125 (1974) [Sov. Phys. JETP **39**, 57 (1974)].

[7] V. N. Ostrovsky and E. A. Solovyov, Zh. Eksp. Teor. Fiz. **66**, 1590 (1974) [Sov. Phys. JETP **39**, 779 (1974)].

[8] V. N. Ostrovsky, Zh. Eksp. Teor. Fiz. **73**, 2077 (1977) [Sov. Phys. JETP **46**, 1088 (1977)].

[9] A. K. Kazansky, J. Phys. B **25**, L381 (1992).

[10] A. K. Kazansky, J. Phys. B **26**, 3869 (1993).

[11] M. I. Chibisov, Opt. Spektrosk. **27**, 9 (1969) [Opt. Spectrosc. **27**, 4 (1969)].

[12] R. L. Becker and A. D. MacKellar, J. Phys. B **17**, 3923 (1984).

[13] Th. Wormann, Z. Roller-Lutz, and H. O. Lutz, Phys. Rev. A **47**, 1594 (1993).

[14] T. Ehrenreich, J. C. Day, S. B. Hansen, E. Horsdal-Pedersen, K. B. MacAdam, and K. S. Mogensen, J. Phys. B **27**, L383 (1994); S. B. Hansen, T. Ehrenreich, E. Horsdal-Petersen, K. B. MacAdam, and L. J. Dube, Phys. Rev. Lett. **71**, 1522 (1993).