J. Phys. B: At. Mol. Opt. Phys. 24 (1991) L127–L132. Printed in the UK

LETTER TO THE EDITOR

Free electron model for collisional angular momentum mixing of high Rydberg atoms

B Kaulakys†

I Physikalisches Institut Universität Giessen, Heinrich-Buff-Ring 16, D-6300 Giessen, Federal Republic of Germany

Received 14 December 1990

Abstract. Simple analytical expressions for the cross sections of $nl \to n'l'$ transitions from Rydberg–neutral inelastic collisions are obtained on the basis of the free electron model for electron–perturber scattering. The dependences of the electron–perturber scattering amplitude on the electron momentum and scattering angle are allowed for. The analytical results agree well with available numerical calculations. The analysis of the equations obtained yields a conclusion that the cross sections at $l \leqslant l'$ depend weakly on l and l' for degenerate states and are proportional to the statistical weights of the final states for transitions with large energy defects.

There has been considerable interest in collisional processes involving Rydberg atoms for some fifteen years, reflecting the progress in experimental laser spectroscopy. Various theoretical investigations of state-changing collisions between Rydberg atoms and neutral atomic or molecular targets have been made (see, e.g., Stebbings and Dunning 1983, Kaulakys and Serapinas 1989 and references therein). Simple analytical expressions have been obtained for the cross sections of elastic broadening and shift of the Rydberg levels (Omont 1977, Kaulakys 1984), for the cross sections of $nl \to n'$ transitions, where n' is a hydrogenic manifold (Gounand and Petitjean 1984, Petitjean and Gounand 1984, Kaulakys 1985, 1986, Lebedev and Marchenko 1985, 1986, 1987) in collisions between the Rydberg atom and a structureless neutral atomic particle. The free electron model based on the analysis of the binary encounter of the Rydberg electron with an incident particle (Kaulakys 1986) has been generalized for inelastic collisions of Rydberg atoms with molecules (Kaulakys 1988).

The theory of collisional transitions between states of Rydberg atoms with the definite orbital quantum number l' of the final Rydberg state, i.e. the theory of the process

$$\mathrm{A}(nl) + \mathrm{B} \to \mathrm{A}(n'l') + \mathrm{B} \tag{1}$$

where $\mathrm{A}(nl)$ is the Rydberg atom in the nl-state and B is the atomic particle, is developed considerably less. There have been only numerical calculations of the cross sections for the process (1) in the scattering-length approximation or with the inclusion of the second term in the expansion of the electron–perturber (e–B) scattering amplitude $f_e(p, \vartheta)$ in powers of the electron momentum p (Derouard and Lombardi 1978,

† Alexander von Humboldt Foundation Research Fellow 1990/91. Permanent address: Institute of Theoretical Physics and Astronomy, Lithuanian Academy of Sciences, 232600 Vilnius, Lithuania.

0953-4075/91/050127+06$03.50

Matsuzawa 1979, Sasano *et al* 1983, Sato and Matsuzawa 1985, Yoshizawa and Matsuzawa 1985). Although, as far as we know, there are no experimental results for the cross sections of the specific $nl \to n'l'$ transitions, the knowledge of the cross sections and regularities of the processes (1) are needed: the transitions (1) govern the populations of the Rydberg nl states and are closely connected with the different observed broadenings and shifts of the various Rydberg series (ns, np and nd) and various fine-structure lines (Kachru *et al* 1980, Thompson *et al* 1987, Borstel *et al* 1988, Hermann 1988, Heber *et al* 1988). One can also refer to the papers by Sirko and Rosiński (1986, 1987) which are devoted to the theoretical investigation of a collisional fine-structure mixing of the highly excited states.

In this paper, on the basis of the free electron model we obtain simple analytical expressions for the cross sections of the process (1), taking into account the dependence of the e–B scattering amplitude on the electron momentum and scattering angle and investigate the dependence of the cross sections on the parameters of the problem. Our calculations are similar to those for a $nl \to n'$ transition in the free electron model (Kaulakys 1986). We assume that the electron–perturber scattering is described by the free electron scattering amplitude, and the transitions between the Rydberg states are due to the change of the kinetic energy and momentum of the electron in the collision with the atomic particle B. We choose the coordinate frame such that the electron momentum $\boldsymbol{p}$ before e–B scattering is directed along the z axis and the electron radius vector $\boldsymbol{r}$ is in the xz plane. The laws of energy and momentum conservation in the elastic e–B scattering yield

$$\varepsilon = 2vp\sin(\vartheta/2)\cos\gamma \qquad \cos\gamma = -\sin(\vartheta/2)\cos\vartheta_a + \cos(\vartheta/2)\sin\vartheta_a\cos(\varphi-\varphi_a) \tag{2}$$

$$J'^2 = J'^2_m \sin^2\chi' \qquad \cos\chi' = \cos\chi\cos\vartheta + \sin\chi\sin\vartheta\cos\varphi. \tag{3}$$

Here ε is the energy transferred to the electron in e–B scattering, J' is the electron angular momentum after e–B scattering, $J'_m = p'r = (n'-1+\frac{1}{2}) \simeq n'$ is the maximal angular momentum of the electron in the n' manifold, ϑ_a and φ_a are the angles of the A(nl)–B collision velocity $\boldsymbol{v}$; ϑ and φ are the e–B scattering angles while χ and χ' are the angles between $\boldsymbol{r}$ and $\boldsymbol{p}$ and $\boldsymbol{r}$ and $\boldsymbol{p}'$, respectively.

At first, we determine the averaged over the velocity directions of the atom B, differential cross section $\mathrm{d}^2\sigma_{e\text{-}B}(p)/\mathrm{d}\varepsilon\,\mathrm{d}J'^2$ for the transfer of the energy ε and receiving angular momentum J' by the electron in the e–B scattering. By analogy with Kaulakys (1986) the differential cross section can be obtained by integrating the squared modulus of the e–B scattering amplitude $|f_e(p,\vartheta)|^2$ over the scattering angles ϑ and φ and averaging over the angles ϑ_a and φ_a, under the condition that the electron had acquired the energy ε and angular momentum J'

$$\frac{\mathrm{d}^2\sigma_{e\text{-}B}(p)}{\mathrm{d}\varepsilon\,\mathrm{d}J'^2} = \frac{1}{4\pi}\int |f_e(p,\vartheta)|^2 \delta\left(\varepsilon - 2vp\sin\frac{\vartheta}{2}\cos\gamma\right)\delta(J'^2 - J'^2_m\sin^2\chi') \times \sin\vartheta\sin\vartheta_a\,\mathrm{d}\vartheta\,\mathrm{d}\vartheta_a\,\mathrm{d}\varphi\,\mathrm{d}\varphi_a. \tag{4}$$

The differential cross section for the energy and angular momentum transfer to the Rydberg atom A(nl) in collision with the perturber B, $\mathrm{d}^2\sigma_{A\text{-}B}/\mathrm{d}\varepsilon\,\mathrm{d}J'^2$, is related to the cross section (4) by the relationship (see Kaulakys (1986) for an exhaustive explanation)

$$\frac{\mathrm{d}^2\sigma_{A\text{-}B}}{\mathrm{d}\varepsilon\,\mathrm{d}J'^2} = \frac{1}{v}\int_0^\infty \frac{\mathrm{d}^2\sigma_{e\text{-}B}(p)}{\mathrm{d}\varepsilon\,\mathrm{d}J'^2}|g_{nl}(p)|^2 p^3\,\mathrm{d}p \tag{5}$$

where $g_{nl}(p)$ is the radial wavefunction of the Rydberg electron in momentum space.

Integrating equation (4) first over φ_a, then over ϑ_a and φ, substituting it into equation (5) and in the usual way passing from the continuous variables ε and J'^2 to the discrete ones n' and l', we have (see Kaulakys 1986)

$$\sigma_{nl,n'l'} = \int_{p_t}^{\infty} \sigma(p)|g_{nl}(p)|^2 p^2\, \mathrm{d}p \qquad p_t = \frac{|\Delta E_{nl,n'l'}|}{2v} \tag{6}$$

$$\sigma(p) = \frac{(2l'+1)\sqrt{2}}{2v^2 n'^5} \times \left[\int_{x_1}^{x_t^{(2)}} \frac{|f_e(p,x)|^2\,\mathrm{d}x}{[(1-x)(x_2-x)(x-x_1)]^{1/2}} + \int_{-x_2}^{x_t^{(1)}} \frac{|f_e(p,x)|^2\,\mathrm{d}x}{[(1-x)(-x_1-x)(x_2+x)]^{1/2}}\right]. \tag{7}$$

Here

$$x = \cos\vartheta \qquad x_t^{1,2} = \min(1-2p_t^2/p^2, \mp x_{1,2})$$
$$x_{1,2} = \{[n^2-(l+\tfrac{1}{2})^2]^{1/2}[n'^2-(l'+\tfrac{1}{2})^2]^{1/2} \mp (l+\tfrac{1}{2})(l'+\tfrac{1}{2})\}/nn'. \tag{8}$$

Equations (6)–(8) constitute the solution of the problem of expressing the cross sections of $nl \to n'l'$ transitions (1) in terms of the e–B scattering amplitude. Let us analyse these expressions.

Integration of equation (7) over l' results to the cross section for $nl \to n'$ transition (Kaulakys 1986)

$$\sigma_{nl,n'} = \frac{\pi}{v^2 n'^3} \int_{p_t}^{\infty} \mathrm{d}p |g_{nl}(p)|^2 p^2 \int_{\vartheta_t}^{\pi} |f_e(p,\vartheta)|^2 \cos\frac{\vartheta}{2}\,\mathrm{d}\vartheta$$
$$\vartheta_t = 2\sin^{-1}\left(\frac{p_t}{p}\right). \tag{9}$$

Expression (9) may also be derived from the impulse approximation (Kaulakys 1985, Lebedev and Marchenko 1986).

For isotropic e–B scattering (s scattering) expression (7) can be integrated up

$$\sigma(p) = \frac{(2l'+1)\sqrt{2}}{v^2 n'^5} |f_s(p)|^2 \left[\frac{F(\varphi_1, k_1)}{(1-x_1)^{1/2}} + \frac{F(\varphi_2, k_2)}{(1+x_2)^{1/2}}\right] \tag{10}$$

where $F(\varphi, k)$ is the elliptic integral of the first kind and

$$k_{1,2} = \left(\frac{x_2-x_1}{1\mp x_{1,2}}\right)^{1/2} \qquad \varphi_{1,2} = \sin^{-1}\left(\frac{x_t^{(2,1)} \mp x_{1,2}}{x_2-x_1}\right)^{1/2}. \tag{11}$$

The cross section takes a particularly simple form for transitions without energy defect, $\Delta E_{nl,n'l'} = 0$, i.e. for $n' = n$ of hydrogenic states. In such a case equations (6) and (10) yield

$$\sigma_{nl,nl'} = \frac{(2l'+1)\sqrt{2}}{v^2 n^5} \overline{|f_s(p)|^2} \left[\frac{K(k_1)}{(1-x_1)^{1/2}} + \frac{K(k_2)}{(1+x_2)^{1/2}}\right] \tag{12}$$

$$\overline{|f_s(p)|^2} = \int_0^{\infty} |f_s(p)|^2 |g_{nl}(p)|^2 p^2\,\mathrm{d}p \qquad \Delta E_{nl,nl'} = 0 \tag{13}$$

where K is the complete elliptic integral of the first kind. In the scattering length approximation, $|f_s(p)|^2 = L^2$, and for $l, l' \ll n$ the expression (12) may be written in the following form

$$\sigma_{nl,nl'} = \frac{2\pi L^2}{v^2 n^4} C_{l,l'} \qquad C_{l,l'} \simeq \frac{2l'+1}{\pi(l+l'+1)} K(k_1) \qquad k_1 = \frac{(2l+1)^{1/2}(2l'+1)^{1/2}}{l+l'+1}. \tag{14}$$

Using the asymptotic expression $K(k)=\frac{1}{2}\ln[16/(1-k^2)]$ as $k\to 1$, one obtains†

$$C_{l,l'}=\frac{2l'+1}{\pi(l+l'+1)}\ln\frac{4(l+l'+1)}{|l'-l|}\qquad 1\leqslant|l'-l|\ll l+l'+1\qquad l,l'\ll n \tag{15}$$

$$C_{l,l}=[1+\ln 4(2l+1)]/\pi. \tag{16}$$

Using the expression $K(k)\simeq\pi/2$ if $k\ll 1$, we have from equation (14)

$$C_{l,l'}\simeq\begin{cases}1 & \text{for } l\ll l'\ll n\\ (2l'+1)/(2l+1) & \text{for } l'\ll l\ll n.\end{cases} \tag{17}$$

It follows from equation (12) that $C_{l,l'}\simeq 1$, if $l'\sim n$. Note the relationship $C_{l',l}=C_{l,l'}(2l+1)/(2l'+1)$, which follows from the condition of a detailed balance.

The completed analysis yields a conclusion that the cross section for $nl\to nl'$ transitions if $l\leqslant l'$, $l\ll n$ and $\Delta E_{nl,nl'}=0$, depends very weakly on l and l'. It follows from the structure of expression (7) that the same conclusion is correct not only for s scattering but for p and d scattering, too. Note that this conclusion is right only if the free electron approximation is valid. For low principal quantum numbers, $n\ll(|L|/v)^{1/3}$, the $nl\to nl'$ transitions may be investigated in the adiabatic approximation (Kaulakys 1982). Such investigation indicates the significant dependence of the cross sections on l and l'.

The earlier results of numerical calculations for the cross sections $\sigma_{nl,nl'}$ by a quasiclassical method (Derouard and Lombardi 1978) and in the impulse approximation (Matsuzawa 1979) turn out to be the partial cases of the conclusions following from equations (12)–(17). A comparison of the values of the coefficients $C_{l,l'}$ according to equations (14)–(16) with the available numerical results, is given in table 1. The agreement of the analytical results (12)–(16) with the numerical quasiclassical (Derouard and Lombardie 1978) and impulse (Matsuzawa 1984) approximations and the analytical expression for the elastic scattering cross section (Kaulakys 1984) is, as a rule, within the limits of 10–20%.

As follows from equations (6)–(11) the cross sections for $nl\to n'l'$ transitions with the energy defect of the transition $\Delta E_{nl,n'l'}\neq 0$ are smaller than for transitions between degenerate states. The analysis of equations (6) and (10) in the scattering length approximation yields

$$\sigma_{nl,n'l'}\simeq\frac{2\pi L^2(2l'+1)}{v^2n'^5}I^{s}_{nl}(\xi)\qquad \xi=n^*p_t\gtrsim 1\qquad l\ll n \tag{18}$$

where the integral

$$I^{s}_{nl}(\xi)=\int_{p_t}^{\infty}|g_{nl}(p)|^2(p-p_t)p\,\mathrm{d}p$$

has been introduced and shown graphically by Kaulakys (1985, 1986, 1988). According to equation (18) the cross sections of $nl\to n'l'$ transitions with large energy defects, contrary to the cross sections for transitions between degenerate states, at $l\leqslant l'$ are proportional to the statistical weights of the final states. This agrees with the results of numerical calculations (Sasano *et al* 1983, Sato and Matsuzawa 1985).

† For $l'=l$ the integral $K(k)$ logarithmically diverges. However, this divergence may be avoided by the averaging of the coefficient $C_{l,l'}$ over $|l'-l|$ in the interval $(-1, 1)$. Such averaging means, that to the definite l, there corresponds not a precise angle χ but an interval $\Delta\chi=2/n$.

Table 1. Comparison of the coefficients $C_{l,l'}$, according to equations (14)-(16), with numerical calculations by a quasiclassical method for $13d \to 13l'$ transitions (Derouard and Lombardi 1978) and in the impulse approximation (Matsuzawa 1979).

	$C_{2,l'}$				$C_{l',l'}$	
l'	Equation (14)	Equation (15)	Derouard and Lombardi (1978)	Matsuzawa (1979)	Equation (16)	Matsuzawa (1979)
0	0.23	0.19	0.22	0.23	0.76	0.58
1	0.75	0.66	0.69	0.70	1.11	1.03
2	1.27†		1.33	1.28	1.27	1.28
3	1.25	1.18	1.29	1.32	1.38	1.46
4	1.23	1.08	1.20	1.38	1.46	
5	1.20	1.04	1.10		1.52	
6	1.18	1.01	1.02		1.58	
7	1.17	0.99	0.93		1.62	
8	1.16	0.98	0.88		1.66	
9	1.16	0.97	0.84		1.70	
10	1.15	0.96	0.82		1.73	
11	1.14	0.96	0.77		1.76	
12	1.14	0.95	0.76		1.78	

† From equation (16).

In most cases one measures experimentally only the cross sections for quenching on nl states with small l. Such cross sections are determined by transitions to the nearest n' hydrogenic manifold with the smallest transition energy defect, $\Delta E_{nl,n'} = \min(\{\delta_l\}n^{*-3}, [1-\{\delta_l\}]n^{*-3})$, where $\{\delta_l\}$ is the fractional part of the quantum defect. Some of the $n'l'$ states with small $l=0, 1, \ldots, l_0-1$ are separated from the manifold n' due to the quantum defects, while the states with $l = l_0, l_0+1, \ldots, n-1$ are degenerate. According to the above analysis the cross section for the transition from the nl state to the level n' with $l' \geqslant l_0$ can be written in the form

$$\sigma_{nl,n'}^{(l_0)} = \beta\sigma_{nl,n'} \qquad \beta \simeq \begin{cases} 1-l_0/n' & \xi \leqslant 1 \\ 1-(l_0/n')^2 & \xi \geqslant 1. \end{cases} \tag{19}$$

At $\{\delta_l\} \simeq 0.5$, transitions to two groups of states with $n' \simeq n^* \mp 0.5$ are significant, and the quenching cross section for the nl state is the sum of two cross sections of type (19). The cross section (19) together with the elastic scattering cross section $\sigma_{nl,nl}$ makes up the broadening cross section for the nl state.

Summarizing, the free electron model based on an analysis of a binary collision of the Rydberg electron with an incident atomic particle (Kaulakys 1986) is suitable for investigation of the $nl \to n'l'$ transitions and enables us to derive simple analytical expressions for the cross sections. In this case, the cross sections of the processes are given by the electron–perturber scattering amplitude, with allowance for the dependence on the electron momentum and scattering angle.

The cross sections for transitions between degenerate states at $l \leqslant l'$ depend weakly on l and l', while for transitions with large energy defects are proportional to the statistical weights of the final states. The extension of the free electron model for m changing and fine-structure mixing collisions is desirable and, in our opinion, possible.

The author is indebted to the A van Humboldt Foundation for the award of a scholarship and to Professors G Hermann and A Scharmann for their hospitality at Giessen.

References

Derouard J and Lombardi M 1978 *J. Phys. B: At. Mol. Phys.* **11** 3875-86

Gounand F and Petitjean L 1984 *Phys. Rev.* A **30** 61-70

Heber K-D, West P J and Matthias E 1988 *J. Phys. D: Appl. Phys.* **21** S63-6

Hermann G 1988 *Phys. Lett.* **133A** 225-30

Kachru R, Mossberg T W and Hartmann S R 1980 *Phys. Rev.* **21** 1124-33

Kaulakys B 1982 *Liet. Fiz. Rinkinys* **22** (5) 22-31 (1982 *Sov. Phys.-Collect: Litovskii Fizicheskii Sbornik (Allerton)* **22** (5) 16-23)

—— 1984 *J. Phys. B: At. Mol. Phys.* **17** 4485-97

—— 1985 *J. Phys. B: At. Mol. Phys.* **18** L167-70

—— 1986 *Zh. Eksp. Teor. Fiz.* **91** 391-403 (1986 *Sov. Phys.-JETP* **64** 229-35)

—— 1988 *Khim. Fiz.* **7** 1443-50 (*Sov. J. Chem. Phys.* 7)

Kaulakys B and Serapinas P 1989 *Spectral Line Shapes* vol 5 (Wroclaw, Poland: Ossolineum) pp 437-58

Lebedev V S and Marchenko V S 1985 *Zh. Eksp. Teor. Fiz.* **88** 754-70 (1985 *Sov. Phys.-JETP* **61** 443-52)

—— 1986 *Zh. Eksp. Teor. Fiz.* **91** 428-44 (1986 *Sov. Phys.-JETP* **64** 251-60)

—— 1987 *J. Phys. B: At. Mol. Phys.* **20** 6041-64

Matsuzawa M 1979 *J. Phys. B: At. Mol. Phys.* **12** 3743-61

—— 1984 *J. Phys. B: At. Mol. Phys.* **17** 1930

Omont A 1977 *J. Physique* **38** 1343-59

Petitjean L and Gounand F 1984 *Phys. Rev.* A **30** 2946-57

Sasano K, Sato Y and Matsuzawa M 1983 *Phys. Rev.* A **27** 2421-30

Sato Y and Matsuzawa M 1985 *Phys. Rev.* A **31** 1366-74

Sirko L and Rosiński K 1986 *J. Phys. B: At. Mol. Phys.* **19** L279-84

—— 1987 *J. Phys. B: At. Mol. Phys.* **20** L487-92

Stebbings R F and Dunning F B 1983 *Rydberg States of Atoms and Molecules* (Cambridge: Cambridge University Press)

Thompson D C, Kammermayer E, Stoicheff B P and Weinberger E 1987 *Phys. Rev.* A **36** 2134-41

von Borstel M, Hermann G and Lasnitschka G 1988 *Z. Phys.* D **9** 15-25

Yoshizawa T and Matsuzawa M 1985 *J. Phys. Soc. Japan* **54** 918-27