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LETTER TO THE EDITOR

Dependence of collisional broadening and shift of Rydberg levels on the angular momentum of the state

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Abstract. A theoretical analysis of the collisional broadening and shift of Rydberg levels with angular momenta $J \geqslant 1$ taking into account the anisotropy of the Rydberg–perturber potential is presented. The symmetry of the problem is used for the calculation of the collision S matrix in a semiclassical approximation with rectilinear trajectories. The obtained expressions for the broadening and shift cross sections allow an explanation of the observed differences between the broadening and shift of the anisotropic np, nd and $n\mathrm{P}_{3/2}$ levels in comparison with those for the spherical ns and $n\mathrm{P}_{1/2}$ states

Collisional processes involving Rydberg atoms remain the subject of active researches (Bielski *et al* 1991, Borodin *et al* 1991, Kaulakys 1991, Lebedev 1991, Łukaszewski and Jackowska 1991, Sun and West 1990, Sun *et al* 1991). During the last fifteen years there has been considerable progress in the studies of interaction and collisions between Rydberg atoms and neutral perturbers, especially in the theory of collisional processes. Thus, broadening and shift of Rydberg levels by elastic collisions with rare-gas atoms may be described for low gas pressures by the impact theory and in a first approximation taking into account only the isotropic part of the interaction potential (Kaulakys 1984). However, later experimental and theoretical investigations (Borstel *et al* 1988, Hermann 1988, Kaulakys 1991) indicate the influence of the anisotropy of the Rydberg–perturber potential on the collisional processes of Rydberg atoms with neutral perturbers.

It is the purpose of this letter to present a theoretical analysis of the collisional broadening and shift of the degenerate Rydberg levels with angular momenta $J \geqslant 1$ taking into account the anisotropy of the Rydberg–perturber potential and to explain the experimentally observed differences (Kachru *et al* 1980, Thompson *et al* 1987, Borstel *et al* 1988, Bielski *et al* 1991) between the broadening and shift of the np, nd and $n\mathrm{P}_{3/2}$ levels in comparison with those of the ns and $n\mathrm{P}_{1/2}$ levels.

The broadening and shift of an optical line corresponding to the transition between a low-lying (e.g. ground state) and a Rydberg state is mostly determined by the perturbation of the Rydberg state. The impact broadening and shift cross sections σ' and σ'' of the degenerate level with angular momentum J in the semiclassical theory are defined by expressions (Omont 1977, Sobelman *et al* 1981)

$$\sigma' - \mathrm{i}\sigma'' = 2\pi \int \Pi(b) b \, \mathrm{d}b \tag{1}$$

$$\Pi = 1 - (2J+1)^{-1} \operatorname{Tr} S(b) \tag{2}$$

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where S is the collision S matrix which connects the wavefunctions before collision and after collision ψ and ψ' by the relation $\psi' = S\psi$ (b is the impact parameter). Thus, the main problem in the theory of broadening and shift of spectral lines associated with transitions between the ground and highly excited states is the calculation of the collision matrix for the Rydberg states.

The S-matrix elements are asymptotic solutions of the standard coupled-channel equations of the time-dependent perturbation theory. It should be mentioned that the coupled-channel calculations for the angular momentum mixing of Rydberg states have been presented in the work of Hickman (1978, 1979, 1981). Recently the coupled equations have been derived and used for the calculations of self-broadening of singlet and triplet lines of helium (Mullamphy *et al* 1991, Leo *et al* 1992). Note that, in general, due to the dependence of the interaction potential on the projection of the angular momentun on the diatomic axis and rotation of the diatomic axis in the collision process, the system of coupled-channel equations is bulky and complicated. Therefore, the investigation of dependences of solutions on the parameters of the problem or analytical solution of the equations even in the first-order perturbation theory is, as a rule, inaccessible. In this letter in order to simplify the problem and to obtain analytical expressions for the cross sections we make use of the symmetry of the problem and properties of the coupling terms.

As the expressions (1) and (2) are rotation invariant, the matrix elements of S may be expressed in any frame of reference. The most convenient is a collision frame of reference with the z-axis directed opposite to the collision velocity v and the y-axis opposite to the impact parameter b (see figure 1). Then, introducing the wavefunctions of the Rydberg atom symmetrized over the sign of projection of the angular momentum (Kaulakys 1979)

$$\chi^{\pm}_{\alpha JM} = \sqrt{\tfrac{1}{2}}(\chi_{\alpha JM} \pm \chi_{\alpha J-M}) \qquad M > 0$$
$$\chi^{+}_{\alpha J0} = \chi_{\alpha J0} \qquad \chi^{-}_{\alpha J0} = 0 \tag{3}$$

one can simplify the solution of the problem. Here J and M label the total angular momentum and its projection on the z-axis, and α denotes the other indices of the state. Using the properties of the rotation matrix for rotation through an angle β about

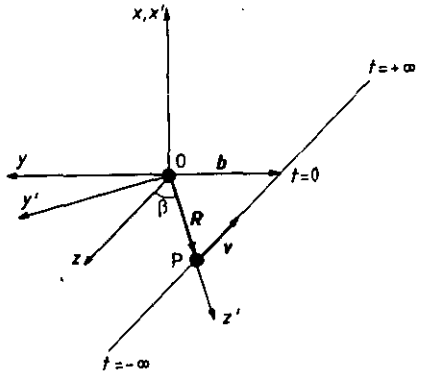

Figure 1. Description of collision between the Rydberg atom O and perturber P, with velocity v and impact parameter b, in terms of the fixed frame $Oxyz$ and rotating frame $Ox'y'z'$.

the x-axis (Jucys and Badzaitis 1965)

$$D^{(J)}_{M\mu}(\beta) = D^{(J)}_{-M-\mu}(\beta) = D^{(J)}_{\mu M}(\beta)$$
$$= \mathrm{i}^{\mu-M} \sum_r (-1)^r \frac{[(J+M)!(J-M)!(J+\mu)!(J-\mu)!]^{1/2}}{r!(\mu-M+r)!(J+M-r)!(J-\mu-r)!} \tag{4}$$
$$\times (\sin\tfrac{1}{2}\beta)^{2r-M+\mu}(\cos\tfrac{1}{2}\beta)^{2J-2r+M-\mu}$$

we obtain the transformation equations for the wavefunctions (3)

$$\varphi^{\pm}_{\alpha JM} = \sum_{\mu\geqslant 0} D^{(J)\pm}_{\mu M}(\beta)\chi^{\pm}_{\alpha JM} \qquad \chi^{\pm}_{\alpha JM} = \sum_{\mu\geqslant 0} [D^{(J)\pm}_{M\mu}(\beta)]^* \varphi^{\pm}_{\alpha J\mu} \tag{5}$$

where

$$\begin{aligned}
&D^{(J)\pm}_{M\mu}(\beta) = D^{(J)}_{M\mu}(\beta) \pm D^{(J)}_{-M\mu}(\beta) && M\mu \neq 0\\
&D^{(J)+}_{0\mu}(\beta) = \sqrt{2}D^{(J)}_{0\mu}(\beta) && \mu \neq 0\\
&D^{(J)+}_{M0}(\beta) = \sqrt{2}D^{(J)}_{M0}(\beta) && M \neq 0\\
&D^{(J)+}_{00}(\beta) = D^{(J)}_{00}(\beta) && M, \mu = 0\\
&D^{(J)-}_{M\mu}(\beta) = 0 && M\mu = 0.
\end{aligned} \tag{6}$$

If angle β is the angle between the z-axis and the direction to the perturber, i.e. $\beta = \cos^{-1}(vt/R(t))$ (for the rectilinear trajectory $R = (b^2+v^2t^2)^{1/2}$), then equations (5) and (6) represent the transformations of the wavefunctions $\chi^{\pm}_{\alpha JM}$ in the fixed (laboratory) frame to the wavefunctions $\varphi^{\pm}_{\alpha JM}$ in the rotating (molecular) frame and backwards.

The eigenfunction $\psi(t)$ of the Hamiltonian H_0+V satisfying the initial condition $\psi(t_0) = \chi^{\pm}_{\alpha JM}$ can be written in the form

$$\psi(t) = \sum_{M'} S^{\pm}_{M'M}\chi^{\pm}_{\alpha JM'} \qquad S^{\pm}_{M'M}(t_0) = \delta_{M',M} \tag{7}$$

where the coefficients of expansion $S^{\pm}_{M'M}$ satisfy the system of equations (Kaulakys 1979)

$$\mathrm{i}\dot{S}^{\pm}_{M'M} = \sum_{M''} S^{\pm}_{M''M} \sum_{\mu} D^{(J)\pm}_{M'\mu}(\beta)[D^{(J)\pm}_{M''\mu}(\beta)]^* \langle \varphi^{\pm}_{\alpha J\mu}|V|\varphi^{\pm}_{\alpha J\mu}\rangle \tag{8}$$

without coupling between symmetric and antisymmetric wavefunctions. Therefore, the system of equations for the matrix elements of S split into two subsystems which simplify the solution of the dynamical part of the problem. Note, that

$$\begin{aligned}
&S^{\pm}_{M'M} = S_{M'M} \pm S_{-M'M} \qquad S^{+}_{M'0} = \sqrt{2}S_{M'0} \qquad S^{+}_{0M} = \sqrt{2}S_{0M} \qquad M, M' \neq 0\\
&S^{+}_{00} = S_{00} \qquad S^{-}_{M'0} = S^{-}_{0M} = 0\\
&\mathrm{Tr}\, S = \mathrm{Tr}\, S^{+} + \mathrm{Tr}\, S^{-} \qquad t_0 \to -\infty,\ t \to +\infty.
\end{aligned} \tag{9}$$

In the following we mainly restrict our consideration to the collisional process described by the Fermi potential $V_F = 2\pi L\delta(\boldsymbol{r}-\boldsymbol{R})$ for the interaction of the perturber with the Rydberg electron, where L is the scattering length for the electron-perturber scattering. From the rotational properties of the Rydberg atom's wavefunctions we have for the one-electron $|nlm\rangle$ state

$$V_{nlm}(R) = \langle \varphi_{nlm}|V_F|\varphi_{nlm}\rangle = \langle \varphi^{\pm}_{nlm}|V_F|\varphi^{\pm}_{nlm}\rangle = \delta_{m,0}(2l+1)V_{nl}(R) \tag{10}$$

and for the one-electron $|njm_j\rangle$ state

$$V_{njm_j} = \delta_{m_j,\pm 1/2}(j+\tfrac{1}{2})\,V_{nl}(R) \tag{11}$$

where $V_{nl}(R) = \frac{1}{2}LR_{nl}^{\,2}(R)$ is the isotropic part of the Fermi potential with $R_{nl}(r)$ being the radial part of the Rydberg electron wavefunction (see Kaulakys 1984, Hermann 1988). It follows from equations (6) and (8) that there is no perturbation of the χ^{-}_{nlm} states while the perturbation of the $\chi^{\pm}_{njm_j}$ states does not depend on the symmetry of the wavefunctions, i.e. $S^{-}_{mm} = 1$ and $S^{-}_{m_jm_j} = S^{+}_{m_jm_j}$. This allows the reduction of equation (2) into

$$\Pi_{nl}(V_F) = \frac{1}{2l+1}\sum_{m=0}^{l}(1-S^{+}_{mm}) \qquad \Pi_{nj}(V_F) = \frac{1}{j+\frac{1}{2}}\sum_{m_j=1/2}^{j}(1-S^{+}_{m_jm_j}) \tag{12}$$

and equations (8) into

$$i\dot{S}^{+}_{m'm} = (2l+1)\,V_{nl}(R)\sum_{m''} D^{(l)+}_{m'0}(\beta)[D^{(l)+}_{m''0}(\beta)]^{*}S^{+}_{m''m} \tag{13}$$

$$i\dot{S}^{+}_{m'_jm_j} = (j+\tfrac{1}{2})\,V_{nl}(R)\sum_{m''_j} D^{(j)+}_{m'_j1/2}(\beta)[D^{(j)+}_{m''_j1/2}(\beta)]^{*}S^{+}_{m''_jm_j}. \tag{14}$$

We see that, in general, there is a coupling between the matrix elements $S^{+}_{M'M}$ with different M' and, therefore, the calculation of the S^{+} matrix is a complicated problem. However, the coupling coefficients of the matrix elements $S^{+}_{M'M}$ and $S^{+}_{M''M}$ with $M'' \neq M'$ are, as a rule, oscillating functions of the angle β and so the transitions between different M' are ineffective and less important than the adiabatic perturbations of the diagonal matrix elements. In such an approximation the matrix elements S^{+}_{MM} may be written in the following form

$$S^{+}_{MM} = e^{-i\eta^{J}_{M}} \qquad \eta^{l}_{m} = A^{l}_{m}(2l+1)\eta_e(b) \qquad \eta^{j}_{m_j} = A^{j}_{m_j}(j+\tfrac{1}{2})\eta_e(b) \tag{15}$$

where $\eta_e(b) = -L/(2vn^{*3}\sqrt{b})$ is the semiclassical phaseshift due to the isotropic part of the Fermi potential $V_{nl}(R)$ (Kaulakys 1984), with n^{*} being the effective principal quantum number of the Rydberg state. The coefficients A^{J}_{M} satisfy the normalization conditions $\Sigma_M A^{J}_{M} = 1$ and according to equations (13) and (14) in a stationary phase approximation may be expressed as

$$A^{l}_{m} = |D^{(l)+}_{m0}(\bar{\beta})|^2 \qquad A^{j}_{m_j} = |D^{(j)+}_{m_j1/2}(\bar{\beta})|^2. \tag{16}$$

Here the angle $\bar{\beta}$ (in general a function of the impact parameter b) is some characteristic angle of the trajectory from the region of the effective Rydberg–perturber interaction.

In the paper by Hermann (1988) it was assumed that only states with $m = 0$ and $m_j = \pm\frac{1}{2}$ are perturbed and the rotation of the interatomic axis was not taken into account. This results in the relatively large broadening and shift difference between $n\mathrm{P}_{1/2}$ and $n\mathrm{P}_{3/2}$ states with intermediate principal quantum numbers. Note, that such an approximation corresponds to the assumption $\bar{\beta} = 0$. However, in our coordinate frame the Rydberg–perturber interaction potential is significant when the angle β is in the interval $\pi/2 - \cos^{-1}(b/2n^{*2}) < \beta < \pi/2 + \cos^{-1}(b/2n^{*2})$, and most of the contribution to the phase $\eta_M{}^{J}$ is from the region of the trajectory where $\beta \approx \pi/2$. The coefficients $A^{l}_{m}(b)$ and $A^{j}_{m_j}(b)$ may be calculated from equations (4), (6) and (16). For instance we have

$$A^{l}_{m}(\tfrac{1}{2}\pi) = \begin{cases} \dfrac{(2-\delta_{m,0})(l-m-1)!!(l+m-1)!!}{2^{l}[\frac{1}{2}(l-m)]![\frac{1}{2}(l+m)]!} & l-m = 2k \\ 0 & l-m = 2k+1,\ k = 0, 1, 2, \ldots \end{cases} \tag{17}$$

and the special values

$$A^{s} = A_1^{p} = A_{1/2}^{1/2} = 1 \qquad A_0^{p} = A_1^{d} = 0$$
$$A_2^{d} = A_{3/2}^{3/2} = \tfrac{3}{4} \qquad A_0^{d} = A_{1/2}^{3/2} = \tfrac{1}{4}. \tag{18}$$

The whole potential of the interaction between the Rydberg atom and the neutral atomic particle consists of the polarization attractions and the short-range interaction between the Rydberg electron and perturber. Therefore, according to Kaulakys (1984) the total phaseshift may be written as

$$\eta_{JM}^{\pm}(b) \simeq \begin{cases} \eta_c(b) + \eta_M^J(b) & b \ll n^{*2} \\ \eta_c(b) & b \gg n^{*2},\ A_M^J = 0 \\ \eta_M^J(b) & b \gg n^{*2},\ A_M^J \neq 0 \end{cases} \tag{19}$$

where $\eta_c = \pi\alpha/4vb^3$ is the phaseshift due to the polarization attraction between the perturber and core of the Rydberg atom with α being the polarizability of the perturber. Note, that for the χ_{nlm}^{-} states the phase due to the Fermi potential $\eta_m^{l-} = 0$ and $S_{mm}^{-} = \exp(-i\eta_c)$, $m > 0$. As a result from equations (1), (2), (9), (12), (15) and (19) we have the expressions for the broadening or shift cross sections

$$\sigma(nl) = \frac{1}{2l+1}\left(l\sigma_c + \sum_{m=0}^{l} \sigma(\alpha, (2l+1)A_m^l L) \right) \tag{20}$$

$$\sigma(nj) = \frac{1}{j+\frac{1}{2}} \sum_{m_j=1/2}^{j} \sigma(\alpha, (j+\tfrac{1}{2})A_{m_j}^j L) \tag{21}$$

where $\sigma_c = \sigma(\alpha, 0)$ is the broadening or shift cross section due to the polarization interaction, i.e. $\sigma_c' = 5.7\ (\alpha/2v)^{2/3}$ or $\sigma_c'' = -\sqrt{3}\sigma_c'$ and $\sigma(\alpha, CL)$ is the broadening or shift cross section due to the superposition of polarization potentials and the Fermi pseudopotential calculated according to equations (26)–(29) from Kaulakys (1984), replacing L by CL. Moreover, σ' in the above-mentioned paper and σ'' in the paper by Thompson *et al* (1987) are averaged over a Maxwellian velocity distribution while the cross sections for a modified Fermi potential taking into account the finite size of the perturber may by estimated as well (Hermann 1988).

It should be noted that expressions (20) and (21) describe the broadening and shift of the levels when l–s coupling may be neglected in the collision process and the contribution from the fine-structure mixing to the broadening is negligible, respectively. From analysis of equations (20) and (21) we can easily draw some conclusions. For instance, the broadening cross sections of the anisotropic nd states for collisions with noble gas atoms may be as much as half those of spherical ns or $n\mathrm{P}_{1/2}$ states if $n^* \leqslant 1.4n_1^*$ and higher if $n^* \geqslant n_2^*$, where $n_1^* = (|L|/4v)^{1/4}$ and $n_2^* = (|L|/\alpha^{1/6}v^{5/6})^{1/3}$. This is in agreement with the experimental observations of Kachru *et al* (1980) and Bielski *et al* (1991). A similar effect may be observed for np and $n\mathrm{P}_{3/2}$ states as well. The absolute values of the shift cross sections for the anisotropic np, nd and $n\mathrm{P}_{3/2}$ states with $n^* \geqslant 1.2\ n_1^*$ are lower than that of the spherical ns and $n\mathrm{P}_{1/2}$ states. The curves representing the shift cross sections as functions of n^* are shifted to the higher n^* by a factor 1.3 n^* for np and nd states and by a factor 1.07 n^* for $n\mathrm{P}_{3/2}$ states in comparison with those for ns and $n\mathrm{P}_{1/2}$ states. This agrees with the experimental results of Thompson *et al* (1987) and Borstel *et al* (1988). According to equations (15), (17) and (20), the broadening cross sections of nl states due to the electron–perturber interaction for $n^* \gg n_1^*$ increase logarithmically with l, which coincides with the conclusion of Kaulakys (1991) for the elastic cross sections.

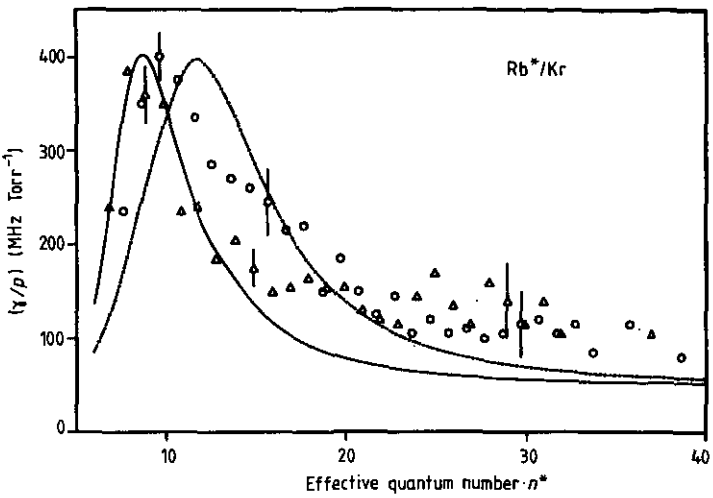

Figure 2. Broadening rates for Rb(nS) and Rb(nd) perturbed by Kr. The symbols indicate the experimental results of Thompson *et al* (1987) for nS(△) and nD(○) states ($T = 530$ K). The full and chain curves shown the theoretical calculations according to equation (20) with $L = -4.0$ and $\alpha = 16.74$ au, for nS and nD states respectively.

Figure 2 illustrates the results of calculations and comparison with experiment. Note that for high principal quantum numbers n the influence of the inelastic collisions to the broadening is important but not taken into account in the present theory. From the side of small n the theory is valid until the Fermi potential approximation for the interaction of the perturber with the Rydberg electron is suitable (see also the discussion by Kaulakys 1984 and Hermann 1988).

In addition, the S matrix obtained in this letter may be used for the calculations of the collisional relaxation of the polarization of the Rydberg states.

Summarizing, a consistent approach for the theoretical analysis of the collisional broadening and shift of the degenerate Rydberg levels with angular momenta $J \geqslant 1$ which simplify the solution of the problem is presented. The calculated cross sections with allowance for the anisotropy of the Rydberg perturber potential explain the experimental observations for the broadening and shift of the anisotropic np, nd and $n\mathrm{P}_{3/2}$ Rydberg levels.

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