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SOME REMARKS AND CALCULATIONS CONCERNING COLLISIONAL FINE STRUCTURE MIXING IN ALKALI METAL ATOMS*

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The analysis of all existing theoretical and experimental results concerning collisional fine structure (FS) mixing, suggesting that their agreement depends on FS separation and FS components intensity anomaly, showed that the test of the theoretical model should be made on sodium atoms. Therefore, the mixing cross sections for the nP ($n = 6 \div 24$) states of sodium atoms colliding with noble gas atoms, N_2 and sodium atoms in the ground state have been calculated theoretically. Cross sections also for the lowest nP states of Na and Rb atoms have been estimated.

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1. Introduction

In the recent review [1] of not solved problems of interactions and collisions between Rydberg atoms and neutral perturbers problems of collisional fine structure (FS) mixing (collisional transition $nLJ - nLJ'$) were omitted. The FS mixing in higher excited states though belonging to relatively simple and at the same time rather fundamental phenomena has not been, as yet, sufficiently investigated either experimentally nor theoretically. The resonance states of alkali atoms [2] and a few of a little higher excited nP states of K ($n = 5$) [3], Rb ($n = 6 \div 7$) [4] and Cs ($n = 7 \div 8$) [4, 5] are the exception. For higher nD excited states experimental results exist only for Rb ($n = 6 \div 9$) [6] and Cs ($n = 6 \div 13$) [7, 8, 9]. There were many successful attemps of theoretical description of the FS mixing in the lowest states of alkali metal atoms (first of all sodium) colliding with noble gas

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atoms (e.g. the recent paper [10]). As regards the FS mixing in Rydberg states, only our model of quasifree Rydberg electron given in [11] exists. It has indeed a general character but it allows a more exact calculation of J-mixing cross sections σ_m for $n\mathrm{P}_{1/2}$ states only. In the case of other series as nD one can calculate practically only the upper and lower limits of σ_m converging, however, for higher n. The model was satisfactorily verified experimentally for the nD ($n = 6 \div 9$) states of Rb atoms colliding with noble gas atoms [6], for $n > 9$ almost no experimental data are available. The model also appears to be correct for the nD states ($11 \leq n \leq 15$) in the process $\mathrm{Cs}(n\mathrm{D})+\mathrm{Cs}(6\mathrm{S}_{1/2})$ [11] (for $n < 11$ there are no calculations, for $n > 15$ there are no experiments). An indirect positive test of the model was given by the experiment with line broadening in collisions: $\mathrm{K}(n\mathrm{P})+\mathrm{K}(4\mathrm{S})$, $n = 18 \div 23$ and $\mathrm{Cs}(n\mathrm{D})+\mathrm{Cs}(6\mathrm{S})$, $n = 11 \div 22$ [12]. The theoretical broadening cross sections were calculated using among others cross sections evaluated by means of the quasifree Rydberg electron model. However, in the case of collisions between Cs(nD, $n = 8 \div 9$) and noble gas atoms the ratio of theoretical to experimental cross section appeared to be about 1 to 5 depending on the kind of noble gas and on the principal quantum number value n [9]. So, our model seems to be not sufficiently good there. Some results, mentioned above, were nevertheless encouraging, so that σ_m's were calculated [13] for $n\mathrm{P}_{1/2}$ states of K ($n = 8 \div 24$) and Rb atoms ($n = 10 \div 24$) colliding with noble gas atoms and N_2 and for collisions $\mathrm{K}(n\mathrm{P}_{1/2})+\mathrm{K}(4\mathrm{S}_{1/2})$, $n = 10 \div 24$ and $\mathrm{Rb}(n\mathrm{P}_{1/2})+\mathrm{Rb}(5\mathrm{S}_{1/2})$, $n = 12 \div 24$, applying the same model. Unfortunately, there have been no experimental data to be compared with. In fact, some experimental results exist for the lowest n for nP states of Na [2], K [2, 3] and Rb [4], but it seems that our model, requiring among others the average radius $< \mathrm{r_e} >$ of the Rydberg electron orbit to be much greater than the radius ρ of the sphere of its interaction with a perturber, is not applicable to these cases. For the lowest n a limit of this condition is attained. In spite of this, looking for arguments that an experiment concerning J-mixing collisions in Na atoms would be the best practical test of the model, the ratio $\sigma_{\mathrm{th}}/\sigma_{\mathrm{exp}}$ for the lowest states of Na and Rb have also been estimated. It was additionally interesting for us to confirm the limit of applicability of our model. Afterwards from an analysis of all existing theoretical and experimental results, the conclusion has followed: the possible discrepancy between the theoretical and the experimental results is connected with the FS separation being too great (which violates the condition of quasielasticity of collisions) and the anomaly intensity of FS components (not taken into account in calculations) being too strong. Therefore we present here the FS mixing cross section calculations we perfomed for nP ($n = 6 \div 24$) doublets of sodium which are distinguished by a sufficiently small FS separation, a small FS intensity anomaly and are well separated from levels of other series (nS, nD, . .). It may be hoped that a future experiment of measuring σ_m for nP states of sodium will give further confirmation of our model.

2. Evaluations

As it is known the collision of a Rydberg alkali atom with a perturber in the ground state at thermal energy can be modelled from the point of view of the FS

mixing as consisting of two independent collisional processes: the atomic core of an alkali metal atom collides with a perturber B, and an excited electron e collides with the perturber B [11]. Moreover, it has been established that the contribution to the mixing cross section from the core-perturber collision can usually be neglected as far as mixing and depopulation collisions are considered [14].

Our paper presents a theoretical evaluation of the σ_m in the intermediate Rydberg $n\mathrm{P}_{1/2}$ ($n = 6 \div 24$) states of Na: $\mathrm{Na}(n\mathrm{P}_{1/2})+\mathrm{B}\rightarrow\mathrm{Na}(n\mathrm{P}_{3/2})+\mathrm{B}$, where B denotes noble gas atoms, N_2 and ground state Na atoms. Additionally for the reasons mentioned above the ratios $\sigma_{\mathrm{th}}/\sigma_{\mathrm{exp}}$ for He as a perturber in the case of the 3P state of Na and $6\div7$ P states of Rb were estimated.

According to the results of [13] the total elastic and inelastic cross section $Q_{n\mathrm{P}_{1/2}}(V)$ in the $n\mathrm{P}_{1/2}$ state can be expressed by the formula (atomic units are used):

$$Q_{n\mathrm{P}_{1/2}}(V) = 2\pi \int_0^\infty b[1-\exp(1-\frac{4}{V}\langle v_e\rangle_{n^*\mathrm{P}}\langle\sigma_e\rangle_{n^*\mathrm{P}}\frac{1}{4\pi}\int_{-\infty}^{\infty} R^2_{n^*\mathrm{P}}((b^2+s^2)^{1/2})\mathrm{d}s)]\mathrm{d}b \tag{1}$$

where $\langle v_e\rangle_{n^*\mathrm{P}}$ is the average velocity of the $n^*\mathrm{P}_{1/2}$ electron ($n^* = n-\delta_L$), $\langle\sigma_e\rangle_{n^*\mathrm{P}}$ is the total cross section for scattering of e on B averaged over the quantum mechanical distribution of the electron velocity in the nP state, $R_{n^*\mathrm{P}}$ is the radial part of the atomic wavefunction, V is the velocity of the Rydberg atom relative to the perturber, b is the collisional impact parameter and s measures the position of the perturber along its trajectory.

As in [13] we concentrate on the $\mathrm{P}_{1/2}$ state because for this state an exact calculation of the total elastic and inelastic cross section $Q_{n\mathrm{P}_{1/2}}(V)$ is possible. For the $\mathrm{P}_{3/2}$ state only estimations of the upper and lower limits of the cross section are possible because of practical reasons.

The average velocities $\langle v_e\rangle_{n^*\mathrm{P}}$ were evaluated from the formula [13]:

$$\langle v_e\rangle_{n^*\mathrm{P}} = 1/(1.590n^* - 0.677). \tag{2}$$

The values of the quantum defect $\delta_{\mathrm{P}} = 0.86$ for $n\mathrm{P}_{1/2}$ states of Na and $\delta_{\mathrm{P}} = 2.66$ for $n\mathrm{P}_{1/2}$ states of Rb have been taken from Lorentzen and Niemax [15].

The averaged total scattering cross sections $\langle\sigma_e\rangle_{n^*\mathrm{P}}$ for Na ($n = 6\div24$) atoms colliding with noble gas atoms and N_2 corresponding to the $\langle v_e\rangle_{n^*\mathrm{P}}$ values were obtained by interpolating the $\langle\sigma_e\rangle_{n^*\mathrm{D}}$ data given in [16]. The values of $\langle\sigma_e\rangle_{n^*\mathrm{P}}$ for Na ($n = 3$) colliding with He and for Rb ($n = 6 \div 7$) colliding with He were calculated using data from [17] and averaging them in the range of electron energy 0–12 eV.

Total scattering cross sections for e–Na [18] are available for a range of electron velocities insufficient to calculate averaged cross sections $\langle\sigma_e\rangle_{n^*\mathrm{P}}$. Therefore the total scattering cross sections corresponding to the average electron velocity in the state nP, i.e. $\sigma_e(\langle v_e\rangle_{n^*\mathrm{P}})$ were used.

Calculations of the $Q_{n\mathrm{P}_{1/2}}(V)$ have been performed assuming for V its mean value $\overline{V} = (8kT/\pi\mu)^{1/2}$, where k is the Boltzmann constant, μ — the reduced mass of the system and T — the temperature: 473 K for the Na–noble gas atoms and the N_2 collisions and 523 K for the Na–Na collisions. The semiclassical wave

function has been taken as an approximation for the radial wavefunction [19]. So the FS components intensity anomaly has been neglected.

The FS mixing cross sections $\sigma_{nP_{1/2}\to nP_{3/2}}(\overline{V})$ have been obtained from the relation [13]:

$$\sigma_{nP_J \to nP_{J'}}(V) = \frac{2J'+1}{N} Q_{nP_J}(V), \tag{3}$$

where for the nP doublet $N = \sum_{j=J}^{J'}(2j+1) = 6$.

We take into account only mixing in the nP state excluding other processes, in particular transitions out of the doublet nP, because the separations of the nL–nL' and nL–$n'L'$ levels are sufficiently large. The FS separation of the nP_J levels in relation to the separation from the nearest $(n-1)$D, $(n-1)$F,...states is more than twenty times smaller.

3. Results and discussion

The FS mixing cross sections evaluated for $nP_{1/2}$ states of Na with $n = 6 \div 24$ are presented in Fig. 1. The rise of the cross sections and then decrease with n, characteristic for intermediate n values, is very clearly seen. Steady decreasing of

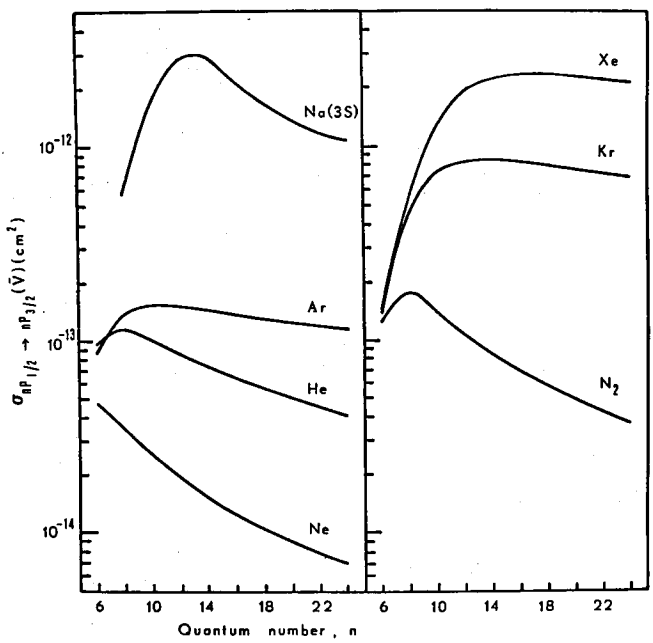

Fig. 1. Theoretical cross sections of FS mixing $\sigma_{nP_{1/2}\to nP_{3/2}}(\overline{V})$ for collisions between Na and noble gas atoms and between Na and N_2 and Na in ground state.

the cross section for Ne even in the region of low n is caused by very small $\langle\sigma_e\rangle_{n^*P}$

cross section and consequently small probability of Na–Ne mixing collisions [13]. The decrease of the cross section $\sigma_{nP_{1/2}\to nP_{3/2}}(\overline{V})$ for Na–Na collisions for $n > 14$ is connected with a decreasing of the total cross section $\sigma_e(\langle v_e\rangle_{n^*P})$ caused by the Ramsauer effect.

In the case of the lowest nP states we have obtained the following results: for the Rb 6P and 7P states the ratio σ_{th}/σ_{exp} is 6 and 3, respectively. For the 3P state in Na the ratio σ_{exp}/σ_{th} is about 4. The results are not satysfying but it is surprising that the discrepancy is not bigger. One can also observe that the discrepancy is relatively smaller for the 3P state of Na than for the corresponding state of Rb with much greater FS separation. The same trend was also observed in the case of higher nD states ($n \leq 9$) where calculations gave much more accurate results for Rb than for Cs atoms [9]. Therefore, it can be suggested that the agreement of σ_{th} and σ_{exp} is better for atoms with smaller FS separation and at the same time weaker FS components intensity anomaly. This observation can be a justification for the performed here calculations of σ_m for nP ($n = 6 \div 24$) states of sodium atoms, presented above. Sodium, having the smallest FS separation, intensity anomaly of FS components and the greatest separation of nP doublets from doublets of other series among heavier alkali metal atoms, seems to be the best candidate for experimental verification of our model.

It seems to be interesting that applying the simple theoretical model of a quasi-free excited electron to the FS mixing one can obtain, even for lower n values and rather great δ_L values, in some cases very good estimates of σ_m for nP and nD series of various kinds of alkali metal atoms. It is evident, however, that there is still a need for more experimental data.

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