

## Collisional broadening of Rydberg states by alkali-metal perturbers

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Collisional broadening of  $nS$  Rydberg states by K, Rb, and Cs atoms is studied using the adiabatic approach for the  $^3\Sigma$  quasimolecular state and impulse approximation for all other contributions to the collisional width. The calculations are based on the use of the low-energy phase shifts for electron scattering by alkali metals obtained from *ab initio* close-coupling calculations and their extrapolation according to the modified effective range theory. We obtain a good agreement for the magnitude of the width with experimental data and satisfactory agreement for the oscillatory part of the width as a function of the principal quantum number. We find that the theory overestimates the amplitude of the oscillations. In the case of Cs as a perturber, the agreement with experimental data is good if we assume the existence of the low-energy  $^3P$  resonance of  $\text{Cs}^-$ . However, recent *ab initio* bound-state and scattering calculations indicate the existence of the  $\text{Cs} (^3P)$  bound state rather than the resonance.

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### I. INTRODUCTION

Studies of collisions of Rydberg atoms with other atoms in the ground state is a very good tool for the investigation of low-energy scattering phase shifts for the collisions of electrons with atoms [1]. For example, the kinetic energy of a Rydberg electron in the state with the principal quantum number  $n=25$  is equal to 0.02 eV which corresponds to the thermal energy region. This region is unavailable for beam experiments, and it causes many uncertainties in data for low-energy electron scattering by atoms, especially for alkali metals. For example, data [2] on momentum-transfer cross sections for the  $e$ -Cs scattering obtained from swarm measurements are in very strong disagreement with theoretical calculations. Therefore, reliable theoretical calculations of Rydberg atom-alkali-metal atom collisions and their comparison with experiments may provide a useful guide. Experimental data [3,4] on collisional broadening of Rydberg states by alkali-metal perturbers are of special interest. In contrast to the data on the rare-gas atoms they exhibit very large broadening cross sections and oscillatory dependence of the broadening and shift on the principal quantum number in the region  $n=25-35$ . The first attempts [5,6] to explain these oscillations were based on the impulse approximation and existence of low-energy  $^3P$  resonance in electron-alkali-metal scattering as suggested by Matsuzawa [7]. However, Fabrikant [8] showed that this explanation implies that the position and width of the resonance strongly disagree with the results of *ab initio* calculations of the scattering phase shifts. On the other hand, *ab initio* phase shifts, substituted in the impulse approximation formula, give good results for sufficiently high  $n$  ( $n > 30$ ). The conclusion was that the impulse approximation cannot explain the oscillatory dependence of broadening and shift on  $n$ .

The physical conditions of the validity of the impulse approximation were discussed elsewhere [7-9]. Here we would like to stress one more point. The impulse approximation is valid if the relative velocity of the Rydberg atom (A)-perturber atom (B) collision is high enough to have only one electron-perturber scattering during one Rydberg-perturber collision. For this purpose we should have

$$V > \frac{r_{e-B}}{T}, \quad (1)$$

where  $r_{e-B}$  is the effective radius of the electron-perturber interaction and  $T \approx 2\pi n^3$  is the period of motion of the Rydberg electron. Therefore the approach fails for low  $V$  or for low  $n$ . The impulse approximation is more justified in the case of nonresonant scattering when the effective radius is roughly equal to the Weiskopf radius [10] (atomic units are used throughout the paper)

$$r_W = \left[ \frac{\pi\alpha}{4v_e} \right]^{1/3}, \quad (2)$$

where  $v_e = 1/n$  is the velocity of the Rydberg electron, and  $\alpha$  is the polarizability of the perturber B. However, in the case of the low-energy  $^3P$  resonance  $r_{e-B}$  becomes greater, and in this case another approach is necessary to describe the collisions.

Recently Borodin and Kazansky [11] suggested the adiabatic mechanism for the collisional broadening of Rydberg states by alkali metals. In contrast to the impulse approximation, this approach assumes the collision velocity to be small enough and considers the multicolisional interaction between the Rydberg electron and the B atom. As a result of this interaction, adiabatic energy curves are formed, and the theory of nonadiabatic transitions can be applied. Using a model approach based on

the Wigner parametrization of the  $^3P$  scattering phase shift, Borodin and Kazansky [11] obtained a satisfactory description of the oscillatory dependence of the broadening cross section of  $n$ .

In the present paper we put these results on a firmer theoretical basis. We calculate the collisional width using the adiabatic approximation for the  $^3P$  contribution and the impulse approximation for all other waves. We use numerical phase shifts obtained by extrapolation of the close-coupling calculations using the modified effective range theory of Fabrikant [8]. Our results have a more quantitative character, although they are still limited by the region of sufficiently high  $n$ , since the impulse approximation fails for low  $n$ , even in the case of non-resonant scattering.

## II. THEORY

We will start with our treatment of the  $^3P$  resonance of the  $B^-$  ion. This state leads to the formation of two quasimolecular states  $^3\Sigma$  and  $^3\Pi$ . These ion states are mixed with the covalent quasimolecular states  $^1\Sigma$  and  $^3\Sigma$  generated by the  $n^2S$  of the Rydberg  $A^{**}$  atom and the  $^2S$  state of the  $B$  atom.

The triplet broadening cross section is given by the expression

$$\sigma'_T = 2\pi \int (1 - \text{Re}S_{\alpha\alpha}) \rho \, d\rho, \quad (3)$$

where  $S_{\alpha\alpha}$  is the diagonal  $S$ -matrix element as a function of the impact parameter  $\rho$ . The collisional width is related to the broadening cross section through the equation

$$\gamma = 2NV\sigma'. \quad (4)$$

The approach of Borodin and Kazansky [11] considers transitions between two states, one of which corresponds to the  $^3P$  resonance state of the ion  $B^-$  and the other to the Rydberg electron in the  $A$  atom. In the two-state approximation

$$S_{\alpha\alpha} = (1 - P^{(a)})e^{2i\delta^{(a)}} + P^{(a)}e^{2i\delta^{(d)}}, \quad (5)$$

where  $P^{(a)}$  is the probability of the inelastic transitions between the adiabatic states,  $\delta^{(a)}$  and  $\delta^{(b)}$  are phases of the system evolution along the adiabatic and diabatic paths.

The energies of the adiabatic states are given by the solutions of the equation [11]

$$\sin\{\pi[\mu_0 + \nu(R)]\} \sin[\pi\nu(R) + \delta_l(p(R))] = W^2(R), \quad (6)$$

where  $\nu(R) = [-2E_{\text{ad}}(R)]^{-1/2}$ ,  $\mu_0$  is the quantum defect of the  $^2S$  state,  $\delta(p)$  is the  $e$ - $B$  scattering phase shift as a function of electron momentum, and

$$W^2(R) = \frac{2l+1}{R^2 p^2} \sin^2 F(R) \sin \delta(p(R)) \sin \pi \mu_0, \quad (7)$$

$$F(R) = 2\nu \int_{R/2\nu^2}^1 (\tau^{-1} - 1)^{1/2} d\tau - \frac{\pi}{4}. \quad (8)$$

Equation (6) was obtained from the Lippman-Schwinger equation for the electron wave function which contains the Coulomb Green's function in the semiclassical repre-

sentation. This representation describes the electron as a free particle having the momentum

$$p(R) = \left[ \frac{2}{R} - \frac{1}{\nu^2} \right]^{1/2}. \quad (9)$$

This assumption implies that the electron's wavelength is large compared to  $r_{e-B}$ . This condition is not very well satisfied in the case of the  $^3P$  resonance when  $r_{e-B} \approx 3/p$ . As we will see below, this deficiency of the approach leads to some overestimation of the oscillatory structure of collisional broadening.

Equation (6) yields the adiabatic energy curves which take into account the interaction between the  $^3P$  resonance state and the whole system of the Rydberg levels. For the solution of the problem it is convenient to introduce the quasiadiabatic energy curves [11] which are determined by the equations

$$\nu_1 = -\mu_0, \quad \nu_2 = -\frac{1}{\pi} \delta_1(p(R)). \quad (10)$$

The first energy curve gives the  $nS$  state and is  $R$  independent, whereas the second curve represents the result of a strong interaction between the  $^3P$  resonant state and the hydrogeniclike multiplet of the Rydberg atom. These quasiadiabatic curves cross at the point  $R_{\text{cr}}(n^*)$  defined by the equation

$$\mu = \frac{1}{\pi} \delta_1(p(n^*, R_{\text{cr}})). \quad (11)$$

The transition rate between the quasiadiabatic states is determined by the mixing parameter

$$\Delta(R) = \frac{1}{\pi(n^*)^3} W(R). \quad (12)$$

For the calculation of the transition probability we use the distorted-wave approximation

$$P^{(d)} = \int_{-\infty}^0 \Delta(z^2 + \rho^2)^{1/2} \times \exp \left[ i \int_{-\infty}^z \Delta E [(\rho^2 + z_1^2)^{1/2}] \frac{1}{v} dz_1 \right] \frac{dz}{v}. \quad (13)$$

The transition probability between the adiabatic states may be obtained from  $P^{(d)}$  according to the Landau-Zener approach

$$P^{(a)} = \exp(-P^{(d)}). \quad (14)$$

The principal contribution to integral (13) is determined by the integration in the vicinity of the crossing point  $R_{\text{cr}}$ . If the mixing parameter  $\Delta$  is  $R$  independent, this approach results in the well-known Landau-Zener formula, but in the present case the mixing parameter  $\Delta(R)$  oscillates as a function of  $R$ , and this oscillatory behavior produces the oscillations of the broadening cross section as a function of  $n$  [11].

We simplified the calculation of integral (13) by keeping only the linear contribution to  $\Delta E$  in the vicinity of the crossing point

$$\Delta E = \frac{dE_1}{dR} (R - R_0). \quad (15)$$

This approximation allows us to take into account the principal contribution and avoid unphysical behavior of the mixing parameter at  $z \rightarrow -\infty$ .

For all quasimolecular terms other than  $^3\Sigma$  we used the impulse approximation for the broadening

$$\gamma = 4\pi N \int w(q) \text{Im} f_q(0) dq, \quad (16)$$

where  $w(q)$  is the momentum distribution of the Rydberg electron, and  $f_q(0)$  is the forward amplitude for the scattering of a free electron with the momentum  $q$  by the perturber averaged over the total spin. The scattering amplitude was calculated using the modified effective range theory as described by Fabrikant [8]. Since the  $^3\Sigma$  contribution has been included in the adiabatic approach, we took only  $\frac{2}{3}$  of the  $^3P$  contribution of  $f_q(0)$ .

### III. RESULTS AND DISCUSSION

The previous calculations [8] of the collisional broadening of Rydberg levels by alkali metals showed that the impulse approximation gives good results for  $n > 30$ . The main purpose of the present paper is to supplement these studies by calculations of the broadening in the most interesting region of intermediate  $n$  ( $15 < n < 30$ ) where the oscillations occur. Since the validity of both the impulse approximation for the non-resonant scattering and our version of the adiabatic approximation for the resonant scattering are limited by sufficiently high  $n$ , our approach does not lead us to expect good results for very low  $n$ .

We will start our discussion from the consideration of the Rb atom as a perturber, since the *ab initio* phase shifts and the scattering lengths for this case give very good results [8] for both broadening and shift in the impulse region. In Fig. 1 we compare our results with two

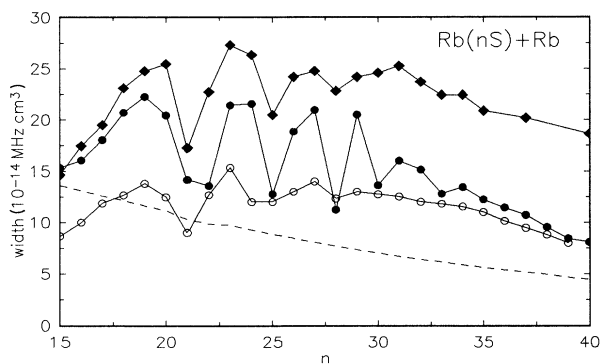


FIG. 1. The dependence of the width per unit number density  $\gamma/N$  for the  $\text{Rb}(nS)$  Rydberg states perturbed by the Rb atoms in the ground state on the principal quantum number  $n$ . Open circles, experimental data of Heinke *et al.* [3]; diamonds, experimental data of Stoicheff and co-workers [4]; dashed line, present theory, contribution of all waves other than  $^3\Sigma$  calculated in the impulse approximation; solid circles, present theory, the  $^3\Sigma$  contribution is added in the adiabatic approximation.

experiments [3,4]. In order to put the results of both experiments on the same scale we used the relation between the pressure and the temperature  $p = Nk_B T$  for  $T = 530$  K. We found that the results of the two experiments disagree by a factor of 2. The calculated width is closer to the results of Heinke *et al.* [3] for large  $n$  and to that of the Thompson, Weinberger, and Stoicheff [4] for low  $n$ . The phase of the oscillations of the theoretical width is in good agreement with both experiments. However, the amplitude of the theoretical oscillations exceeds the experimental amplitudes. As we have suggested in Sec. II, this phenomenon is caused by the quasiclassical representation of the Coulomb Green's function that implies the point electron-perturber interaction. An averaging over the effective range of the *e*-B interaction should smooth the oscillations. It should be emphasized that the assumption about the point *e*-B interaction is necessary in our approach only for the calculation of the Green's function, but not for the inclusion of the *e*-B interaction by itself. More details can be found in Refs. [12,13].

In Fig. 2 we compare our results for the broadening of the K *S* levels by Rb with the experimental data of Heinke *et al.* [3]. Again we find good agreement for the magnitude of width, and reasonable agreement for the phase of the oscillations, but the theoretical amplitude is too large as compared with the experiment.

Let us turn now to the case of the K atom as a perturber. In Fig. 3 we present results for the broadening of K by K. As in the case of Rb-Rb, the results of the two experiments differ by a factor of 2, and the magnitude of the theoretical cross sections is in very good agreement with the results of Heinke *et al.* [3]. However, both the phase and amplitude of the theoretical oscillations disagree with the experiment. The simplest way to fit the theoretical phase to the experimental one is to change the parameters of the  $^3P$  resonance. However, we did not attempt to do that because our treatment of the resonant scattering is too approximate, and there might be some other reasons for the disagreement. In particular, the averaging of the oscillations over the region of the *e*-B interaction mentioned above might give a shift to the phase of the oscillations.

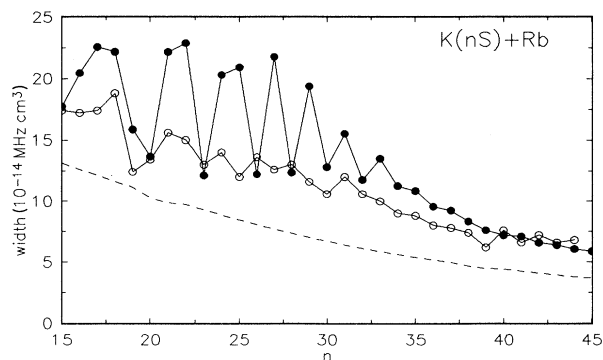


FIG. 2. The same as in Fig. 1 for the perturbation of  $\text{K}(nS)$  states by Rb.

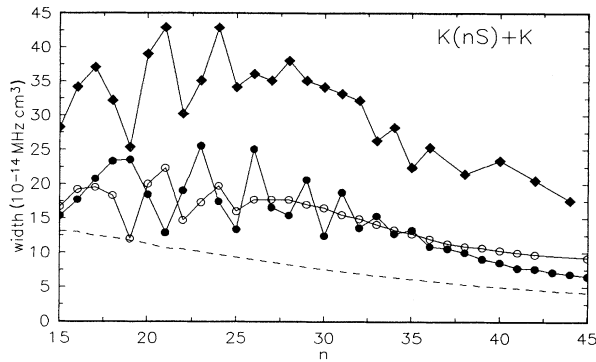


FIG. 3. The same as in Fig. 1 for the perturbation of  $K(nS)$  states by K.

In Fig. 4 we present the results for the broadening of Rb by K. They demonstrate essentially the same features as those in the case of the K-K interaction.

The case of the Cs atom as a perturber is of special interest due to considerable uncertainties in the data for thermal energy electron scattering by Cs. As shown by Fabrikant [8,14], many results of swarm measurements (see, e.g. Refs. [2,15]) of momentum-transfer cross sections for Cs are in a strong disagreement with the theoretical calculations. The most realistic experimental results could be explained [14] if we assume the existence of the low-energy  $^3P$  resonance as in all other alkali metals. However, it has been suggested [16] that due to the large polarizability of the Cs atom it can support the  $^3P$  bound state instead of the resonance. Recent accurate bound-state calculations [17,18] confirmed this assumption and gave values for the energy of the bound state that are quite close to the first estimate [16].

The existence of the  $\text{Cs}^-(^3P)$  bound state strongly reduces the low-energy momentum-transfer cross section, and does not allow for explanation of the results of swarm measurements [2]. Moreover, the existence of the  $^3P$  bound state strongly reduces the collisional broaden-

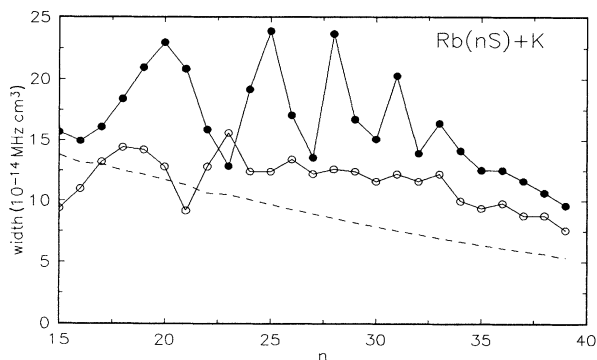


FIG. 4. The same as in Fig. 1 for the perturbation of  $\text{Rb}(nS)$  states by K.

ing of the Rydberg states by Cs in the impulse approximation [8] and in this instance leads to strong disagreement with the experiment. Therefore further investigations of the problem would be of great interest.

Our adiabatic treatment of the  $^3\Sigma$  scattering can also be applied in the case of the  $^3P$  bound state. However, in this case the intersection between the quasiadiabatic potential curves occurs in the classically forbidden region. The Rydberg electron wave function does not oscillate in this region and the oscillations of the width as a function of  $n$  disappear. Therefore, if the experimental oscillations in this case were to occur, our consideration would confirm the existence of the  $^3P$  resonance rather than the bound state.

The experimental data for  $S$  states in the case of Cs as a perturber are more scarce than in the cases considered above. They cover a more narrow range of  $n$ , and do not permit definite conclusions about the existence of the oscillations in the broadening of  $S$  states. However, the oscillations are observed in the broadening of  $\text{Cs}(nD)$  states by Cs. As with calculations in the impulse approximation [8], the magnitude of the width for  $S$  states is in very good agreement with the theory if we assume the existence of the  $^3P$  resonance. In Fig. 5 we present the result of calculations of the width of the Cs Rydberg states perturbed by Cs with the scattering parameters found in Ref. [8] (case C in Table 3). Apparently, the region  $n < 22$  cannot be described by our theory, but in the region  $22 < n < 30$  we have very good agreement with the experiment. Additional experimental data for  $n > 30$  would be highly desirable. On the other hand, since experimental data for higher  $n$  are available for the broadening of  $nD$  states, an extension of the theory to the case of  $nD$  states would be quite useful.

In Fig. 6 we present the data for the Rb atoms perturbed by Cs. Experimental data exist only for  $n < 20$ , which is apparently out of the range of the validity of our theory. Again, experimental data exist for higher  $n$  for broadening of the  $nD$  states.

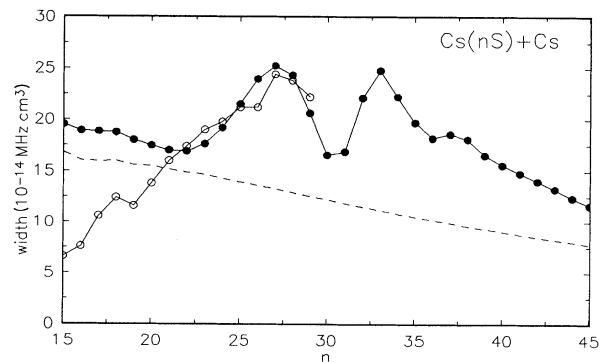


FIG. 5. The same as in Fig. 1 for the perturbation of  $\text{Cs}(nS)$  states by Cs. Calculating the  $^3\Sigma$  contribution to the width we assumed the existence of the  $\text{Cs}^-(^3P)$  resonance with the position  $E = 12.6$  meV and width  $\Gamma = 9.1$  meV (see Ref. [8]).

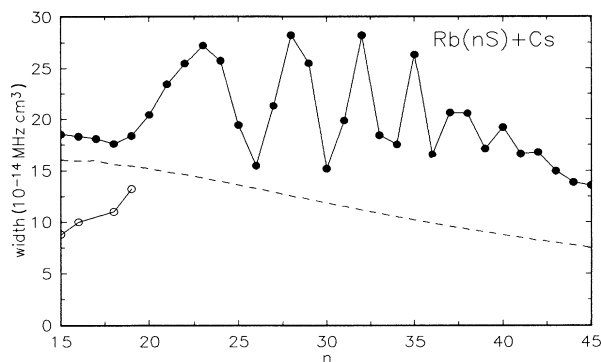


FIG. 6. The same as in Fig. 5 for the perturbation of  $Rb(nS)$  states by Cs.

#### IV. CONCLUSIONS

The results obtained in the present paper improve our understanding of the interaction of Rydberg atoms with alkali metals. The combination of the impulse approximation approach for the nonresonant scattering, and the adiabatic approach of Borodin and Kazansky [11] for the resonant scattering, allows us to obtain a good description of the broadening of the  $nS$  Rydberg levels by alkali metal perturbers at intermediate values of the principal quantum number  $n$  ( $15 < n < 30$  for Rb and K as perturbers and  $20 < n < 30$  for Cs as a perturber). The best

results were obtained for Rb as a perturber. However, even in this case the amplitude of oscillation of the width as a function of  $n$  is too large compared to the experimental data. The reason for that is the approximate treatment of the Coulomb Green's function entering the integral equation for the adiabatic energy of the quasi-molecule  $AB$ . This approximation implies that the radius of the  $e$ -B interaction is small compared to the electron wavelength that is not very well justified for the resonant scattering. We expect that a more precise treatment of the Green's function will lead to smoothing of the oscillations.

The Cs atom as a perturber still remains an interesting and contradictory object. On the one hand, the early prediction [16] and recent *ab initio* calculations [17-19] yield a  $^3P$  bound state for  $Cs^-$ . This is also supported by accurate *ab initio* scattering calculations [19,20]. On the other hand, the swarm measurements [2] and large- $n$  behavior of the width of Rydberg levels perturbed by Cs cannot be explained without an assumption about the existence of the  $^3P$  resonance. Present studies also confirm the existence of the  $^3P$  resonance. Further studies of both transport phenomena in weakly ionized Cs vapors and collisional broadening of Rydberg states by Cs atoms, both experimental and theoretical, are necessary to resolve this contradiction.

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