

A mechanism for exciting oscillations of Rydberg level widths of alkali-metal atoms

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An adiabatic mechanism is proposed for the oscillations in the broadening cross sections when nonhydrogenic Rydberg states of alkali-metal atoms are quenched in an atmosphere of such atoms. The oscillations are due to a low-lying and relatively broad 3P resonance of the quenching atom. The term generated by this resonance crosses the nonhydrogenic levels, and the resulting term splitting is determined by the wave function of the Rydberg electron at the term-crossing point. This wave function oscillates as a function of the principal quantum number n , and this gives rise to the oscillations in the cross sections. This simple picture has had to be significantly extended for the problem discussed in this paper. In particular, a new Landau-Zener type dynamic problem is found to arise, in which oscillations in the term coupling parameter near the crossing point are found to be significant. The results obtained are in qualitative agreement with experimental data for the pairs $K^{**}(n^2S) + Rb$ and $Rb^{**}(n^2S) + Rb$.

1. INTRODUCTION

The collision widths and shifts of the non-hydrogen-like Rydberg nS , nP , and nD levels of alkali-metal atoms in the vapor phase were measured in the 1980s for a wide range of values of the principal quantum number n ($n \geq 10-50$). The oscillations (with varying n) in the spectral characteristics of quenched Rydberg nS and nD states (SCQRS), i.e., level widths and shifts due to collisions between highly excited alkali-metal atoms and similar atoms in the ground state, were reliably recorded for $n \approx 15-30$.¹⁻⁴

Attempts were then made⁵⁻¹⁰ to use the impulse approximation to relate these oscillations to the existence of a weakly-bound quasi-stationary alkali-metal negative ion in the 3P state, but careful analysis has shown¹⁰⁻¹² that the oscillations could only be explained by assuming an anomalously small width Γ_γ for the 3P resonance. In addition, the impulse approximation was found to be generally invalid in the region in which the oscillations appeared, since it could only be used for $n \geq 25-30$, and there are no oscillations in this range. For $n \leq 30$, on the other hand, a better description is achieved by using the adiabatic approximation.

In this paper, we propose a mechanism for the SQRS oscillations, based on the adiabatic approximation, and using the 3P resonance as our starting point. We shall show that this mechanism reproduces correctly the phase of the oscillations and provides a qualitative description of the cross sections.

2. DESCRIPTION OF THE MECHANISM AND QUALITATIVE ESTIMATES

The essence of the mechanism that we propose is as follows. When a Rydberg alkali atom A^{**} approaches another unexcited alkali-metal atom B, the quasistationary 3P state of the ion B^- with energy¹⁾ $E_\gamma = k_\gamma^2/2$ in the presence of the positive ion A^+ becomes stable for nuclear separations $R < E_\gamma^{-1}$. The corresponding ion terms $^3\Sigma$, $^3\Pi$ exhibit a quasi-crossing of the Coulomb and nonhydrogenic (S, P, D) Rydberg covalent levels for $R = R_{cr}(n^*) < E_\gamma^{-1}$ (Fig. 1a). When specific conditions are satisfied, the crossing points $R_{cr}(n^*)$ lie well inside the classically allowed region for the motion of the Rydberg electron (RE) after a certain value of the effective principal quantum number n_0^* ,

i.e., for $n^* > n_0^*$. The term splitting at the quasicrossing point $R_{cr}(n^*)$ is then proportional¹³ to the square of the absolute value of the RE wave function at the point $R_{cr}(n^*)$. Since the phase of this function at the point $R_{cr}(n^*)$ depends on n^* , the probability of a transition between the ionic and covalent terms oscillates as a function of n^* , which gives rise to the oscillations in the broadening cross section σ' and to the shift of Rydberg levels as a function of n .

Let us now estimate the broadening cross section σ' for the nS state of a Rydberg atom. If we ignore the distorting effect of polarization interactions (in both ionic and covalent states), we find that

$$R_{cr}(n^*) = \frac{2n^{*2}}{1+2n^{*2}E_\gamma}. \quad (1)$$

The broadening cross section σ' can be crudely estimated for $n^* > n_0^*$ by substituting $\sigma' \approx \pi R_{cr}^2(n^*)$. Since the characteristic value of $R_{cr}(n^*)$ for alkali metals is of the order of 280 a.u., we find for $n^* = 20$ that $\sigma' \approx 6 \cdot 10^{-12}$ cm², which is of the order of magnitude of the experimental results.¹⁻⁴ Using the criterion proposed in Ref. 14, we then find that

$$\frac{R_{cr}}{2n^{*2}} \leq 1 - \left[\frac{2}{n^{*2}} \right]^{1/3}, \quad (2)$$

which shows that, at the point of transition, the perturbing atom lies in the interior of the corresponding electric orbit, well away from the RE turning point. If we then use (1) and (2), we find that the lower limit n_0^* of the range of values of n^* for which there are oscillations is given by

$$n_0^* \approx (4E_\gamma^3)^{-1/4}, \quad (3)$$

which, for alkali metals with $E_\gamma \sim 10^{-3}$ a.u., gives $n_0^* \approx 13-15$, is in agreement with experiment.

We shall now derive an expression for the broadening cross section σ' , using the two-state approximation, to begin with. With the parametrization employed in Refs. 14 and 15 for the elastic S -matrix, after averaging over the large diabatic phase and rejecting the relatively small dynamic phases¹⁶ we find that the broadening cross section is given by

$$\sigma' = \frac{3\pi}{2} \int_{\rho_0}^{R_{cr}(n^*)} (1-P)\rho \, d\rho + \pi\rho_0^2 \quad (4)$$

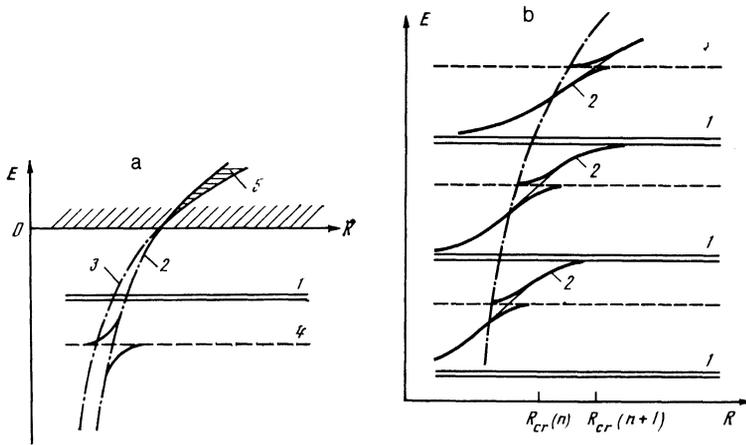


FIG. 1. Coarse (a) and actual (b) energy level curves for the problem considered here: 1—pure Coulomb multiplet, 2—ionic term ${}^3\Sigma$, 3—ionic term ${}^3\Pi$, 4—Rydberg non-hydrogen-like nS (${}^3\Sigma, {}^1\Sigma$) state; the P and D states are also found to split from the Coulomb multiplet, but are not shown in the figure. The limit of the continuous spectrum and the quasistationary 3P state are also shown [ionic configuration (5)]; (b) 1—pure Coulomb multiplet, 2—adiabatic ${}^3\Sigma$ term formed as a result of strong interaction between the ionic ${}^3\Sigma$ term (curve 3) and the Coulomb multiplet as described in the Appendix [cf. (A17)]. We are considering the diabatic crossing of this adiabatic ${}^3\Sigma$ term and the ${}^3\Sigma$ configuration (curve 3) generated by the Rydberg S -state whose crossing parameters are evaluated in the Appendix [cf. (A21) and (A22)].

where P is the probability of a nonadiabatic transition for a single crossing of the nonadiabatic region in the neighborhood of $R_{cr}(n^*)$, and $\rho_0 = (\pi\alpha/4v_\infty)^{1/3}$ is the Weisskopf radius corresponding to the polarization interaction between the atomic core A and the perturbing atom B (α is the probability of atom B). In deriving (4), we took into account the contribution of the polarization interaction between A^+ and B in the covalent ${}^{1,3}\Sigma$ -states of the quasi-molecule $A^{**}(nS) + B$, but ignored the influence of the stable ionic state ${}^1\Sigma$ of the system $A^+ + B^-$ (1S), although it does have a relatively high binding energy, and calculations performed in the impulse approximation show that it can play an important part in the evaluation of δ' for $n \geq 30$.

In the approximation employed in (4), the shift cross section σ'' can be expressed¹⁴⁻¹⁶ in terms of the phases $\delta^{(d)}$, $\delta^{(a)}$ for motion over the diabatic and adiabatic ${}^3\Sigma$ -term that corresponds to the nS configuration. The final result is

$$\sigma'' = \frac{3}{2} \pi \left[\int (1-P) \sin 2\delta^{(a)} \rho \, d\rho - \int (1-P) \sin 2\delta^{(d)} \rho \, d\rho \right] + \sigma_0'' \quad (5)$$

where

$$\sigma_0'' = 2\pi \int \sin 2\delta^{(d)} \rho \, d\rho$$

is the shift cross section due to the polarization interaction between the ion A^+ and the atom B . We shall not analyze the shift cross section σ'' any further because this would require more detailed information about the behavior of the phases $\delta^{(a)}$, $\delta^{(d)}$.

It is interesting to note that (4) can also be obtained in the multilevel approximation in which motion along the ion term is described for $R < R_{cr}(n^*)$ in terms of the effective width $\Gamma(R)$ of the ionic state:

$$\begin{aligned} \sigma' = & \pi\rho_0^2 + \frac{3\pi}{2} \int_{\rho_0}^{R_{cr}(n^*)} (1-P) \rho \, d\rho \\ & - \frac{3\pi}{2} \int_0^{R_{cr}(n^*)} (1-P) \exp \left[- \int_{R'}^{R_{cr}(n^*)} \Gamma(R) \frac{dR}{v_R(R)} \right] \\ & \times (1 - 2 \sin^2 \delta^{(a)}) \rho \, d\rho, \end{aligned} \quad (6)$$

where R' is the left turning point on the diabatic term of R of the ion. It follows from (6) that, when $\delta^{(a)} \gg 1$, and if

$$\int_{R'}^R \Gamma(R) \frac{dR}{v_R(R)} \gg 1$$

expression (6) becomes identical with (4). In other words, the multichannel nature of the collision process has no significant effect on the form of (4).

It is shown in Ref. 17 that, when one oblique term crosses a set of parallel terms, the elastic and inelastic transition probabilities can be calculated in the Landau-Zener approximation. On the other hand, we can use the results obtained in Ref. 13 to find the Landau-Zener parameter ξ and the probability P :

$$\begin{aligned} \xi &= \frac{3\Gamma_r \cos^2 \delta_1^{(0)}}{4\pi E_r n^3 v_R(R_{cr})} \sin^2 \Phi(n^*), \\ P &= \exp[-2\pi\xi] \end{aligned} \quad (7)$$

where Γ_r is the width of the 3P resonance, $\delta_1^{(0)}$ is the corresponding partial phase in potential scattering, $v_R(R_{cr})$ is the radial velocity at the point R_{cr} , and $\Phi(n^*)$ is the quasi-classical phase of the RE wave function at the point $R_{cr}(n^*)$:

$$\Phi(n^*) = 2n^* \left\{ \frac{\pi}{2} - [s_{cr}(1-s_{cr})]^{1/2} - \arctg \left(\frac{s_{cr}}{1-s_{cr}} \right)^{1/2} \right\} - \frac{\pi}{4},$$

in which $s_{cr} = R_{cr}/2n^*$. Substituting (7) in (4), we obtain

$$\begin{aligned} \sigma' = & \frac{3}{4} \pi R_{cr}^2 \left[1 - 2 \left(\frac{\lambda}{v_\infty} \right)^2 \Gamma \left(-2, \frac{\lambda}{v_\infty} \left[1 - \left(\frac{\rho_0}{R_{cr}} \right)^2 \right]^{-1/2} \right) \right] \\ & + \frac{\pi}{4} \rho_0^2, \end{aligned} \quad (8)$$

where v_∞ is the relative velocity of the atoms at infinity, $\lambda = 2\pi\xi v_R(R_{cr})$, and $\Gamma(x,y)$ is the incomplete gamma-function. It is clear from (8) that, when $\xi = 0$, for which $n^* > n_0^*$, the broadening cross section has a minimum value equal to $\pi\rho_0^2$. On the other hand, the maxima of σ' occur for the same values of n^* for which $\sin^2 \Phi(n^*) \sim 1$.

The above discussion is entirely qualitative for two important reasons: first, the method of Ref. 13 was employed in the derivation of (7) and assumes that $\Gamma_r \ll E_r$, whereas we know that $\Gamma_r \sim E_r$ for the alkali-metal atoms. Second the above method leads to oscillations even for $n > 30$, and we know from experiment, and from the impulse approximation, that there are no oscillations in the region. The first difficulty can be obviated by extending the method used in Ref. 13 (see Appendix), and the second is of considerable

theoretical interest because it demands the establishment of a connection between the adiabatic and the impulse approximations.

3. QUANTITATIVE EVALUATION OF THE BROADENING CROSS SECTION

In practice, there is considerable mixing of ionic and Rydberg terms because of the relatively large widths of the quasistationary 3P state of the A^- ion. This is indicated by the fact that, at the pseudocrossing point of the ionic and the isolated Coulomb Rydberg levels (Fig. 1b), the term splitting is of the order of the level separation. The quantity $R_{cr}(n^*)$ that appears in (4) and (5) must therefore be redefined, and must be evaluated from (1) in which E_r must be replaced with the reduced energy \tilde{E}_r of the resonance, defined by (A20) in the Appendix.

The Landau-Zener approximation used in (7) presupposes that the interaction V between the terms is a slowly-varying function over the distance $\Delta R \sim V/\Delta F$ characterizing the size of the transition region. In our case, we have to remember that the effective matrix element between two terms oscillates for sufficiently large n^* (definitely larger than n_0^*) inside this region. Fortunately, however, the corresponding transition probability is low, and this enables us to employ the distorted-wave approximation. We actually use a mixed approach in which the Massey parameter is calculated in the distorted-wave approximation and the transition probability is found from the Landau-Zener formula with the Massey parameter.

In the above approximation, the exponent in the Landau-Zener formula is determined by the probability of transition between the diabatic ionic and covalent $^3\Sigma$ terms, and is given by

$$P^{(d)} \approx 2\pi\xi = \frac{n^4}{v_R^2(R_{cr})} \left| \int \Delta_0(R_{cr}=2n^2S_{cr}) \times \sin \left[2n^* \int_s^1 p(\tau) d\tau - \frac{\pi}{4} \right] \exp \left[i \int_s^1 \Delta H dt \right] ds \right|^2, \quad (9)$$

where $p(\tau) = (\lambda^{-1} - 1)^{1/2}$, $S_{cr} = R_{cr}/2n^2$ and ΔH is the difference between the diabatic terms. The expression for $\Delta_0(R_{cr})$ is given in the Appendix. We now consider the term in the off-diagonal matrix element that is an oscillating function of R , and take the slowly-varying part $\Delta(R)$ to be equal to its value at the point R_{cr} .

Since we have $2n^* \gg 1$, the integral in (9) can readily be evaluated by the method of stationary phase. The position of the points of stationary phase (PSP) is determined by the equation

$$n^* \Delta H(s)/v_R(R_{cr}) = \pm p(s). \quad (10)$$

If we assume, for the sake of simplicity, that $v_R(R_{cr}) = v_\infty$ in (10), and that the dependence of ΔH on s is given by the linear expression $\Delta H = 2n^* \Delta F(R_{cr})(s - s_{cr})$ [the expression for the difference in slopes ΔF of the diabatic terms is given by (A21) in the Appendix], we find that there is little difficulty in analyzing (10). The positive sign in (10) always gives a single real root $s_{cr} < s_1 < 1$, and the equation with the negative sign gives either two roots $0 < s_3 < s_2 < s_{cr}$ or no roots (more precisely, in the latter case, the two roots are complex). Of course, in the second case, both roots lead to

an exponentially small contribution, and the integral (9) is entirely determined by the single transition point. If all the three roots are real, then together with the first root s_1 , they generate an interference pattern for $P^{(d)}$ as a function of the effective quantum number n^* . Finally, in this case, the probability $P^{(d)}$ is given by

$$P^{(d)} = \frac{\pi n^* \Delta_0^2(R_{cr})}{4\lambda v_R^2(R_{cr})} \left| a_1(s_1) \exp[2in^* \Phi_+(s_1)] - ia_2(s_2) \exp[2in^* \Phi_-(s_2)] - a_3(s_3) \exp[2in^* \Phi_-(s_3)] \right|^2, \quad (11)$$

where

$$\begin{aligned} \lambda &= 2n^* \Delta F(R_{cr})/v_R(R_{cr}), \\ a_1(s_1) &= \left(1 + \frac{1}{2\lambda p(s_1) s_1^2} \right)^{-1/2}, \\ a_i(s_i) &= \left| 1 - \frac{1}{2\lambda p(s_i) s_i^2} \right|^{-1/2}, \quad i=2, 3, \\ \Phi_\pm(s) &= \frac{\lambda}{2} (s - s_{cr})^2 \pm \int_s^1 p(\tau) d\tau. \end{aligned}$$

It is important to note that, when $n^* > n_0^*$, we have for the PSP $s_1 \approx s_2 \approx s_{cr}$, $0 < s_3 \ll 1$, so that the point s_2 lies outside the range of validity of the theory. However, since, in this case, $a_1(s_1) \approx a_2(s_2) \approx 1$, $a_3(s_3) \ll 1$, we can use (11) as before, except that the third term in this expression is now small. As n^* increases, the difference $s_1 - s_2$ is found to increase, the oscillations in the matrix element as a function of $R = 2n^*s$ become significant inside the transition region, and the approximation (7) ceases to be valid. The transition from one regime (three PSP) to the other (one real PSP) occurs for a certain boundary value n_b^* defined by the following set of equations:

$$\begin{aligned} \lambda(s_b - s_{cr}) &= -p(s_{cr}), \\ \lambda &= [2p(s_b) s_b^2]^{-1}, \\ \lambda &= 2n_b^* \Delta F/v_\infty. \end{aligned}$$

When $n > n_b^*$, we must put $a_2(s_2) = a_3(s_3) = 0$ in (11), which ensures that the parameter $P^{(d)}$ ceases to oscillate and, after it is substituted in the Landau-Zener formula, the resulting transition probability can be used to find the cross section σ' from (4). The final expression for this cross section is then very similar to the result obtained in Ref. 9 in the impulse approximation.

We now emphasize the physical significance of (10). For $n^* > n_0^*$, it is natural to take the idea of adiabatic terms as our starting point. The product $v_R(R)p(R)$ can then be interpreted as the characteristic frequency of variation of the nonadiabatic interaction over the nuclear separation R . The final diabatic state of the ion can be populated in a number of ways. Up to the crossing point R_{cr} , and if $R_1 > R_{cr}$, the resonance condition $\omega(R_1) = \Delta H(R_1 = 2n^*s_1)$ is satisfied, and we have a transition from the covalent to the diabatic ionic term. This term is populated when $\omega(R_{2,3}) = -\Delta H(R_{2,3})$ with $R_{2,3} < R_{cr}$ (Fig. 2), or when there is a transition from the diabatic covalent term to the diabatic ionic term under resonance conditions. To find the corresponding transition amplitude, we must combine the amplitudes corresponding to these two channels, and this leads to the interference-type oscillations. Equation (10) can also be interpreted in the

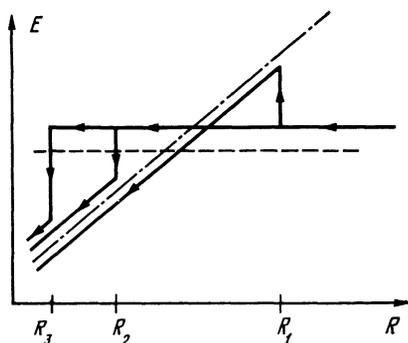


FIG. 2. Three coherent channels for a transition from the covalent $nS(^3\Sigma)$ term to the ionic $^3\Sigma$ state, where the interference between the corresponding contributions to the transition amplitude determines the oscillations in the quenching cross section.

spirit of the impulse approximation, which seems appropriate for $n^* \sim n_b^*$. In the reference frame in which the atom B is at rest, the electron that collides with this atom has the velocity $p \pm v_R(R)$ (the separation of the radial motion of the electron is motivated by the selection rules that arise when the nonadiabatic interaction is evaluated in the Appendix). If we ignore the perturbing effect of the purely Coulomb level (see Fig. 1), we find that the difference ΔH between the diabatic ionic term and the covalent term is given by

$$\Delta H = E_r - 1/R + 1/2n^{*2}.$$

Equation (10) can then be written (to within the small quantity $v_R^2/2$ in the form of the resonance condition

$$E_r = [p(R) \pm v_R(R)]^2/2. \quad (12)$$

The vanishing of the real roots in (10) and (12) with the negative sign signifies the absence of resonance in collisions between the electron and atom B if both travel in the same direction. The transition between the adiabatic and impulse regimes is associated precisely with the fact that the resonance occurs for both directions of motion of the electron relative to atom B. We note that this transition is sensitive to the relative velocity of atoms A^{**} , and B, although it may be difficult to produce a variation in the collision velocity in a wide range.

The expression given by (11) for the transition probability between diabatic states becomes invalid when the two roots s_2, s_3 coincide for $n \sim n_b^*$. The precise evaluation of $P^{(d)}$ in this region demands a more accurate application of the method of stationary phase.¹⁸ We shall not follow this idea any further and simply reproduce in Fig. 3 the calculations performed with and without the smallest PSP $s = s_3$. It is clear that the contribution of this point is significant only in the neighborhood of the transition between the adiabatic and impulse regimes, i.e., for principal quantum numbers n^* of the order of n_b^* , whose typical value is $n_b^* \sim 30$.

Figure 3 shows the calculations performed for $Rb^{**}(nS) + Rb$ and $K^{**}(nS) + Rb$ collisions. The resonance parameters of Rb were taken to be ¹⁹ $\gamma = 6.36$ a.u. and $\varepsilon_0 = 1.2 \cdot 10^{-3}$ a.u. (see the Appendix for the notation). Careful measurements of the broadening cross sections of the nS and nD levels were made in Refs. 3 and 4 at $T \sim 520$ K. It is clear that the calculations satisfactorily reproduce the oscillation structure both in respect of the position of the

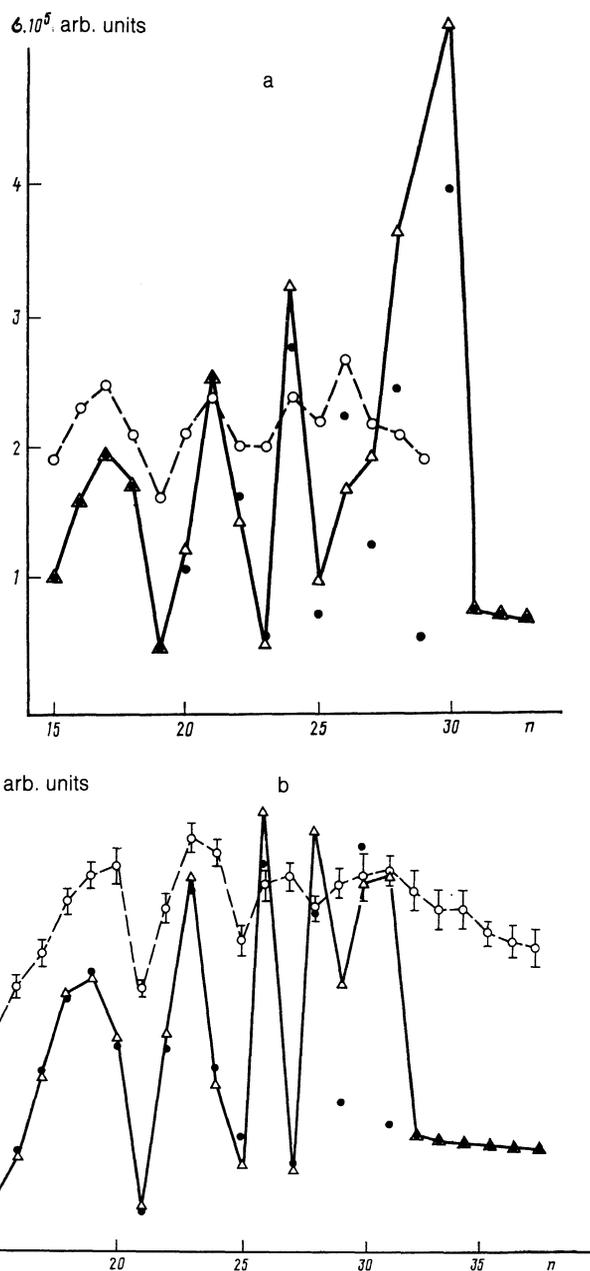


FIG. 3. Quenching cross sections for the nS levels in collisions with rubidium atoms: (a) $K^{**}(n^2S) + Rb$, (b) $Rb^{**}(n^2S) + Rb$. The notation is as follows: \triangle —the contributions due to the three transition points taken into account, \bullet —only the two transition points s_1 and s_2 taken into account, \circ —experimental results (dashed curves) reported in Refs. 3 and 4 for (a) and Ref. 4 for (b).

maxima and minima, and the order of magnitude of the cross sections. The anomalously deep minima should not be taken too seriously: our quenching mechanism is anomalously weak in these cases, and other quenching mechanisms unrelated to oscillations, come into play. These include potential (nonresonance) scattering, largely due to the presence of stable negative ions of the alkali metal in the S state. Allowance for this mechanism can be treated as an independent problem. The importance of potential scattering is also indicated by calculations made in the impulse approximations.^{10,19} In particular, this quenching mechanism may lead to a slower reduction in the measured cross section as compared with theory.

CONCLUSIONS

The mechanism that we have proposed is quite universal and demands only that the "quenching" atom have a quasistationary ionic resonance with low enough binding energies and widths, and that the Rydberg atom have isolated non-hydrogen-like levels. However, if the energy parameters of the resonance are too small, the SCQRS oscillations will be better described by the impulse approximation than by the adiabatic approximation discussed here. It is also important to note that the oscillations in the cross section as a function of the number n of pure Coulomb levels are absent because, in this case, the splitting at the crossing point between the ionic and Coulomb terms is a monotonic function of n (cf. Appendix). We note, by the way, that the SCQRS oscillations arise not only because of the mechanism discussed here, but also by ionization in atomic collisions.²⁰ The oscillations occur for $n^* \sim 10$, and their amplitude is smaller by one or two orders of magnitude than the amplitude of the SCQRS oscillations observed experimentally. As far as the quenching of Coulomb states is concerned, we note that the absence of SCQRS oscillations in this case could serve as confirmation of this mechanism.

In calculating σ , we ignored nonadiabatic transitions due to the rotation of the axes passing through the nuclei, which in our case gives rise to the mixing of the $^3\Sigma$ and $^3\Pi$ states. It was shown in Ref. 21 that this mechanism can play a significant role in the dynamics of transitions between Rydberg states in the intermediate range of values of n^* ($n^* < 30$), but the inclusion of this factor is not a trivial problem.

The parameters of the negative ions of alkali-metal atoms have been measured and calculated in recent years.²²⁻²⁶ It was found that some of these ions can be in a resonant state with energy of the same order as in the case of alkali-metal atoms, e.g., ($\text{Ca}^- (^2P)$ eV for $E_r \sim 5 \cdot 10^{-2}$). Consequently, we may expect that the SCQRS oscillations will arise if the "quenching" atom is a suitably chosen rare-earth atom, say, Ca. An attempt to detect these oscillations was reported in Ref. 27, but was said by the authors to be unsuccessful for experimental reasons.

APPENDIX

1. Equation for the adiabatic terms

In the central-field approximation, the one-electron Green's function of an optical electron of a Rydberg atom is shown by the quantum defect method (CDM) to be²⁸

$$G(\mathbf{r}, \mathbf{r}'; E) = G^{(c)}(\mathbf{r}, \mathbf{r}'; E) + \delta G(\mathbf{r}, \mathbf{r}'; E),$$

where $G^{(c)}(\mathbf{r}, \mathbf{r}'; E)$ is the pure Coulomb Green's function²⁸ and

$$\begin{aligned} \delta G(\mathbf{r}, \mathbf{r}'; E) = & \frac{\nu}{rr'} \sum_{L=0}^{L_0} \frac{\Gamma(1+L-\nu)}{\Gamma(1+L+\nu)} \frac{\sin \pi(\mu_L+L)}{\sin \pi(\nu+\mu_L)} \\ & \times \frac{2L+1}{4\pi} P_L(\mathbf{nn}') W_{\nu, L+1/2} \left(\frac{2r}{\nu} \right) W_{\nu, L+1/2} \left(\frac{2r'}{\nu} \right) \end{aligned}$$

in which $L = 0, \dots, L_0$ are the orbital angular momenta of the nonhydrogenic levels relative to the core of A^+ , $\nu = (-2E)^{-1/2}$, E is the electron energy, $\Gamma(\dots)$ is the gamma function, $W_{\nu, L+1/2}(\dots)$ is the Whittaker function,²⁹ $P_L(\mathbf{nn}')$ is the Legendre polynomial, $\mathbf{n} = \mathbf{r}/r$, $\mathbf{n}' = \mathbf{r}'/r'$, and

μ_L is the quantum defect. We use for $G^{(c)}(\mathbf{r}, \mathbf{r}'; E)$ the representation given in Ref. 30, and write $W_{\nu, L+1/2}(2r/\nu)$ in the quasiclassical form.¹⁴ The Green's function for $\nu \gg 1$, $r, r' < 2n^2$, $R^2 p \gg |\mathbf{r} - \mathbf{r}'|$, $R^2 p \gg |\mathbf{R} - (\mathbf{r} - \mathbf{r}')/2|$, $L^2/\nu^2 \ll 1$ can then be taken in the form

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; E) = & \frac{1}{2\pi |\mathbf{r} - \mathbf{r}'|} \{ \cos[p(R) |\mathbf{r} - \mathbf{r}'|] \\ & - \text{ctg } \pi\nu \sin[p(R) |\mathbf{r} - \mathbf{r}'|] \} \\ & + \frac{1}{2\pi \sin \pi\nu} \sum_{L=0}^{L_0} \frac{(2L+1) \sin \pi\mu_L}{\sin \pi(\mu_L + \nu)} \\ & \times P_L(\mathbf{nn}') \frac{\sin(y + \pi/4)}{rr'} \frac{\sin(y' + \pi/4)}{[p(R)p(R')]^{1/2}}, \end{aligned} \quad (\text{A1})$$

where

$$p(r) = \left(\frac{2}{r} - \frac{1}{\nu^2} \right)^{1/2}, \quad y = 2\nu \int_{r/2\nu^2}^1 (\tau^{-1} - 1)^{1/2} d\tau.$$

The interaction between the Rydberg electron and the perturbing atom B is described by the separable approximation

$$\hat{V}_{eB} = \lambda \langle \vartheta, \varphi, \rho | F_{lm} \rangle \langle F_{lm} | \vartheta', \varphi', \rho' \rangle. |F_{lm}\rangle = |Y_{lm} \chi_l\rangle, \quad (\text{A2})$$

where λ is the coupling constant, l, m are the electron orbital angular momentum and its component along the nuclear axis, $\rho = |\mathbf{r} - \mathbf{R}|$ describes the position of the electron relative to the atom B, (ϑ, φ) are the spherical coordinates of the vector ρ , and χ_l and Y_{lm} are, respectively, the radial and angular harmonics. The parameters \hat{V}_{eB} are chosen so as to reproduce correctly the quantities E_r and Γ_r for the low-energy 3P resonance of the $e + B$ system. If we use the equation for the bound states and the resonances in the field \hat{V}_{eB}

$$\begin{aligned} \frac{1}{2\pi} \left(\langle F_{lm} | \frac{\cos(p|\rho - \rho'|)}{|\rho - \rho'|} | F_{lm} \rangle \right. \\ \left. + i \langle F_{lm} | \frac{\sin(p|\rho - \rho'|)}{|\rho - \rho'|} | F_{lm} \rangle \right) = -\frac{1}{\lambda}, \end{aligned} \quad (\text{A3})$$

we find in the approximation of low momenta p that the equation for the angular momenta l of the resonance assumes the standard form³¹

$$-\varepsilon_0 + 1/2 p^2 + i\gamma p^{2l+1} = 0. \quad (\text{A4})$$

The parameters ε_0 and γ in this expression are given by

$$\begin{aligned} \varepsilon_0 = & \frac{2\pi\lambda^{-1} + \langle F_{lm} | |\rho - \rho'|^{-1} | F_{lm} \rangle}{\langle F_{lm} | |\rho - \rho'| | F_{lm} \rangle}, \\ & 4\pi \left[\int_0^\infty \chi_l(\rho) \rho^{l+2} d\rho \right]^2 \\ \gamma = & - \frac{1}{[(2l+1)!!]^2 \langle F_{lm} | |\rho - \rho'| | F_{lm} \rangle}. \end{aligned} \quad (\text{A5})$$

To simplify these expressions, we confine our attention to the case $m = 0$ and l odd. We now use the method of Ref. 13 to evaluate the terms after the summation sign in (A1) between the center of A^+ and the center of B. For small $p(R)$, the equation $\langle F_{lm} | G | F_{lm} \rangle = \lambda^{-1}$ for the eigenvalues of the hamiltonian of the system $A^{**} + B$ assumes the form

$$\frac{1}{2\pi} \langle F_{l0} | |\rho - \rho'|^{-1} | F_{l0} \rangle - \frac{p^2(R)}{4\pi} \langle F_{l0} | |\rho - \rho'| | F_{l0} \rangle$$

$$- 2 \operatorname{ctg} \pi \nu \frac{p^{2l+1}(R) \left[\int_0^\infty \chi_l(\rho) \rho^{l+2} d\rho \right]^2}{[(2l+1)!!]^2}$$

$$+ \sum_{L=0}^{L_0} \frac{(2L+1) \sin \pi \mu_L}{\sin \pi \nu \sin \pi (\mu_L + \nu)} \frac{2(2L+1)}{[(2L+1)!!]^2}$$

$$\times \frac{p^{2l-1}(R) \sin^2 \Phi(R)}{R^2} \left[\int_0^\infty \chi_l(\rho) \rho^{l+2} d\rho \right]^2 = -\lambda^{-1}, \quad (\text{A6})$$

where

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

If we divide this equation by $-\langle F_{l0} | |\rho - \rho'| | F_{l0} \rangle / 2\pi$, and use the definitions of the parameters ε_0 and γ , we obtain

$$-\varepsilon_0 + \frac{p^2(R)}{2} - \gamma p^{2l+1}(R) \operatorname{ctg} \pi \nu + \sum_{L=0}^{L_0} \frac{(2L+1) \sin \pi \mu_L}{\sin \pi \nu \sin \pi (\mu_L + \nu)}$$

$$\times \frac{(2l+1) \gamma p^{2l+1}(R) \sin^2 \Phi(R)}{R^2 p^2(R)} = 0. \quad (\text{A7})$$

Since the interaction operator \hat{V}_{eB} does not appear explicitly in (A7), and the expression contains only the parameters ε_0 and γ of the 3P resonance, we may conclude that the choice of $\nu_k^{(0)}$ in the form given by (A2) is not a significant restriction on the generality of the final result given by (A7).

2. EVALUATION OF THE MATRIX ELEMENT OF THE NONADIABATIC INTERACTION BETWEEN THE IONIC AND COVALENT TERMS AND THEIR PSEUDOCROSSING PARAMETERS

From now on we ignore the influence of all the nonhydrogenic levels of the atom A^{**} other than the nS level. This means that we retain only the $L=0$ term in the sum over L in (A7). Since we are only interested in the effect of the 3P resonance on the Rydberg levels, we also put $l=1$. We then have

$$[p^2(R)/2 - \varepsilon_0 - \gamma p^3(R) \operatorname{ctg} \pi \nu] \sin \pi (\mu_0 + \nu) = -b \sin \pi \mu_0 / \sin \pi \nu, \quad (\text{A8})$$

where

$$b(\nu, R) = 3\gamma p(R, \nu) \sin^2 \Phi(R) / R^2.$$

Since there is no interaction between the covalent Rydberg nS level $\nu_k^{(0)}$ and the adiabatic term $\nu_c^{(0)}$ that splits from the pure Coulomb level during the interaction with the ionic configuration (Fig. 1b), the energy levels can be determined from the equations

$${}^{1/2} p^2(R, \nu_c^{(0)}) - \varepsilon_0 - \gamma p^3(R, \nu_c^{(0)}) \operatorname{ctg} \pi \nu_c^{(0)} = 0, \quad (\text{A9})$$

$$\sin \pi (\mu_0 + \nu_c^{(0)}) = 0.$$

Near the pseudocrossing point, the right-hand side can be simplified to read

$$b(\nu, R) \sin \pi \mu_0 / \sin \pi \nu \approx (-1)^{n+1} b(n^*, R), \quad (\text{A10})$$

$$\nu_k^{(0)} = n^* = n - \mu_0.$$

When $R \sim R_{cr}$, the shift of the adiabatic Coulomb term $\nu_c^{(0)}$ and of the covalent term $\nu_k^{(0)}$ is much less than unity. Using this result near the pseudocrossing point, we have

$$\sin \pi (\mu_0 + n^* + \nu - n^*) \approx (-1)^n \pi (\nu - n^*), \quad (\text{A11})$$

$${}^{1/2} p^2(R, \nu) - \varepsilon_0 - \gamma p^3(R, \nu) \operatorname{ctg} \pi \nu$$

$$\approx {}^{1/2} p^2(R, \nu_c^{(0)}) - \varepsilon_0 - \gamma p^3(R, \nu_c^{(0)}) \operatorname{ctg} \pi \nu$$

$$\approx \gamma p^3(R, \nu_c^{(0)}) [\operatorname{ctg} \pi \nu_c^{(0)} - \operatorname{ctg} \pi \nu]$$

$$\approx \gamma p^3(R, \nu_c^{(0)}) \pi (\nu - \nu_c^{(0)}) / \sin^2 \pi \nu_c^{(0)}. \quad (\text{A12})$$

Thus, (A8) can finally be reduced to the following quadratic form if we use (A10)–(A12):

$$(\nu - n^*) (\nu - \nu_c^{(0)}) = \frac{b(n^*, R) \sin^2 \pi \nu_c^{(0)}}{\pi^2 \gamma p^3(\nu_c^{(0)}, R)}, \quad (\text{A13})$$

whose solutions are

$$\nu(R) = \frac{1}{2} (n^* + \nu_c^{(0)}) \pm \left[\frac{(\nu_c^{(0)} - n^*)^2}{4} + \frac{b(n^*, R) \sin^2 \pi \nu_c^{(0)}}{\pi^2 \gamma p^3(\nu_c^{(0)}, R)} \right]^{1/2}. \quad (\text{A14})$$

Near the crossing point defined by $\nu_k^{(0)} = n^*$, the splitting ΔE of the adiabatic terms in the matrix element of the nonadiabatic interaction $\Delta(R)$ is

$$\Delta E = \left\{ [2(\nu_c^{(0)}(R))^2]^{-1} - [2n^{*2}]^{-1} \right\}^2$$

$$+ \frac{4b(n^*, R) \sin^2 \pi \nu_c^{(0)}(R)}{\pi^2 n^{*6} \gamma p^3(R, \nu_c^{(0)})} \Bigg\}^{1/2}, \quad (\text{A15})$$

$$\Delta(R) = \frac{2 \sin \pi \nu_c^{(0)}(R)}{\pi n^{*3}} \left[\frac{b(n^*, R)}{\gamma p^3(\nu_c^{(0)}, R)} \right]^{1/2}. \quad (\text{A16})$$

The splitting $\Delta E^{(i)}$ in the neighborhood of the crossing point $R_{cr}^{(i)}$ of the ionic term and the Coulomb level with quantum number n is found by solving the equation obtained from (A9):

$$\Delta \nu \operatorname{tg} \pi \Delta \nu = \gamma n^3 p^3(R, n),$$

where $\Delta \nu = \nu_c^{(0)} - n$, $R_{cr}^{(i)} = 2n^2 / (1 + 2n^2 \varepsilon_0)$. If $\pi \gamma n^3 p^3 \ll 1$, then

$$\Delta E^{(i)}(R, n) = 2 [\gamma p^3(R, n) / \pi n^3]^{1/2}, \quad (\text{A17})$$

whereas for $\pi \gamma n^3 p^3 \gg 1$ we have

$$\Delta E^{(i)}(R, n) = \frac{1}{n^3} - \frac{1}{\pi n^6 \gamma p^3}. \quad (\text{A18})$$

The crossing point $R_{cr}(n^*)$ can be determined by using the real positive root x_0 of (A9) with $\nu_c^{(0)} = n^*$;

$$x^3 + \kappa x^2 - 1 = 0. \quad (\text{A19})$$

where

$$p = [\varepsilon_0 \gamma^{-1} \operatorname{tg} \pi \mu_0]^{1/2} x, \quad \kappa = [(8\gamma^2 \varepsilon_0)^{-1} \operatorname{tg}^2 \pi \mu_0]^{1/2}.$$

We then have

$$\frac{1}{R_{cr}(n^*)} = \frac{1}{2n^{*2}} + E_r, \quad E_r = \frac{1}{2} \left[\frac{\varepsilon_0 \operatorname{tg} \pi \mu_0}{\gamma} \right]^{1/2} x_0^2(\kappa). \quad (\text{A20})$$

At the point $R_{cr}(n^*)$, the difference between the term slopes

$$\Delta F = \left| \frac{d}{dR} (-2\nu^2)^{-1} \right|_{R_{cr}}$$

can be found by differentiating (A9):

$$\Delta F = \frac{1 + 3\gamma p(R_{cr}, n^*) \operatorname{ctg} \pi \mu_0}{R_{cr}^2(n^*) [1 + \pi \gamma p^3(R_{cr}, n^*) n^{*3} / \sin^2 \pi \mu_0 + 3\gamma p(R_{cr}, n^*) \operatorname{ctg} \pi \mu_0]}.$$

For $n^* > n_0^*$, the second term in the denominator of this expression is much smaller than the first or the third, so that

$$\Delta F = \frac{2 \sin^2 \pi \mu_0}{\pi R_{cr}^2(n^*)} \frac{(1 + \frac{3}{4} \Gamma_r \bar{E}_r^{-1} \operatorname{ctg} \pi \mu_0)}{n^{*3} \Gamma_r}, \quad (\text{A21})$$

where $2\gamma p^3(R_{cr}, n^*) = \Gamma_r$, $p^2(R_{cr}, n^*) = 2\hat{E}_r$.

Near the point $R_{cr}(n^*)$, the exchange interaction $\Delta(R)$ can be written in the form

$$\Delta(R) \approx \Delta_0(R_{cr}) \sin \Phi(R, n^*), \quad (\text{A22})$$

where

$$\Delta_0(R_{cr}) = 6^{1/2} [\pi n^{*3} R_{cr} \bar{E}_r^{1/2}]^{-1} \sin \pi \mu_0.$$

In the limit of a very narrow resonance ($\varepsilon_0 \gamma^2 \ll 1$), the reduced parameters \bar{E}_r and Γ_r become equal to ε_0 and $4 \cdot 2^{1/2} \gamma \varepsilon_0^{2/3}$, and the Landau-Zener parameter calculated from (A16) and (A21) becomes identical with the corresponding exponent obtained by the approach proposed in Ref. 13 [cf. (7)].

¹⁾ Here and in what follows we use atomic units.

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