Relation between the broadening of Rydberg levels and resonances in the scattering of slow electrons by atoms

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This paper investigates the contribution of resonance scattering of slow electrons by atoms to the broadening and shift of highly excited atomic levels under the action of pressure. It is shown that the oscillation in the width and shift of *np* levels of Cs in cesium vapor with increasing n and the large widths are determined by the presence of the ^3P resonance having a width $\Gamma \approx 3\times10^{-4}$ eV in the scattering of the electron with an energy $\epsilon_p \approx 7.5\times10^{-4}$ eV by the Cs atom. These parameters are obtained from a comparison of theoretical and experimental data.

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INTRODUCTION

In recent years, interest has increased in the investigation of atoms in highly excited (Rydberg) states. This is associated with some interesting properties of highly excited atoms. The use of them allows one to investigate a series of physical problems on the interaction of atoms and atomic collisions and has also a practical application, in particular, for the selective recording of individual atoms and the separation of isotopes.[1-5] Spectroscopic investigations of the broadening of highly excited atomic levels give information on the amplitude of electron scattering by perturbing atoms. Fermi[6] gave a theoretical explanation of the shift of highly excited levels of atoms located in a foreign gas. According to Fermi theory, the shift Δ of the level with high principal quantum number n is determined by two effects: the scattering of the valence electron by perturbing particles and the polarization of perturbing particles located near the atomic core. The shift on account of scattering Δ_s is determined by the equation

$$\Delta_s = 2\pi LN, \tag{1}$$

where L is the length of electron scattering by perturbing particles and N is the density of perturbing particles. (Atomic system of units $n = e = \hbar = 1$ is used.) Alekseev and Sobelman[7] developed the Fermi theory and showed that the shift Δ and the width γ of a spectral line near the series limit are more precisely determined by the expressions

$$\Delta(n, l) = \Delta_s(n, l) + \Delta_p, \quad \gamma(n, l) = \gamma_s(n, l) + \gamma_p, \tag{2}$$

$$\Delta_s(n, l) = -2\pi N \int \mathrm{Re}\, f_q(0)\, |g_{nl}(0)|^2 q^2 dq, \tag{3}$$

$$\gamma_s(n, l) = 4\pi N \int \mathrm{Im}\, f_q(0)\, |g_{nl}(0)|^2 q^2 dq, \tag{4}$$

$$\gamma_p = 11.4\left(\frac{\alpha}{2}\right)^{2/3} V^{1/3} N, \quad \Delta_p = -\frac{\sqrt{3}}{2}\gamma_p. \tag{5}$$

Here Δ_s and γ_s are the components of the shift and width determined by the scattering of the Rydberg electron by perturbing particles; Δ_p and γ_p are polarization components; $f_q(0)$ is the amplitude of forward scattering of a free electron with momentum q by a perturbing particle; $g_{nl}(q)$ is the radial part of the wave function of the Rydberg electron in the momentum representation; α and V are the polarizability and the velocity of perturbing particles. If the perturbing particles are not spherically symmetrical, it is necessary to introduce in Eqs. (3)–(5) the averaging over orientations and the total spin of the system perturbing atom + electron. The limits of applicability of the given approximation will be discussed.

A review of the latest theoretical and experimental works on the collisions of highly excited atoms with neutral ones is given in Refs. 2 and 3. Summarizing the investigations in this field, it is possible to say that the experiments on the broadening of Rydberg states of alkali metals by inert gases are well described by Eqs. (2)–(5). However, the experimentally measured large widths of the Rydberg states of K and Cs in their own gas[8] have not yet found satisfactory explanation. An inelastic mechanism of broadening, adopted in Ref. 9, allowed one to explain large widths of spectral lines but gave insignificant shifts. The basis of considering such an inelastic mechanism of broadening is not fully under-

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stood.[2] Moreover, as far as we know, there is even no qualitative explanation of the nonmonotonic behavior of the broadening and shift of Cs spectral lines in cesium vapor with increasing principal quantum number n in the range 18–30, which was found in Ref. 8. These phenomena are investigated here.

THEORY

We will investigate the components of the shift and width determined by scattering of a Rydberg electron by perturbing atoms when slow electron scattering by the atom resonances occur. These resonances may correspond to the short-lived quasi-stationary states of a negative ion, whose existence for Li, Na, and K was predicted in a theoretical paper.[10] The possibility of investigating such resonances by the broadening and shift of the Rydberg series of neutral atoms was reported briefly in an earlier paper.[11]

Using Ref. 12, the radial part of the Rydberg electron wave function in the momentum representation can be written in the form

$$g_{nl}(q)=(-i)^l\sqrt{\frac{2\nu_n}{\pi}}\frac{\nu_n(1-\cos\theta)^2}{\sin(\theta-\pi)}\sin\left[\nu_n(\theta-\pi)+l\frac{\pi}{2}\right], \tag{6}$$

$$\cos\theta=(\nu_n^2q^2-1)(\nu_n^2q^2+1)^{-1}. \tag{7}$$

Here ν_n is the effective principal quantum number. Equation (6) is valid for $\nu_n \gg l$; it is not valid for $\theta \to 0$ or $\theta \to \pi$. Using the equations from Ref. 12, we can obtain a more accurate expression for $g_{nl}(q)$ which is valid for $\theta \to \pi$. This will be useful in further discussion.

After simple calculations, we have

$$g_{nl}(q)=-i\sqrt{\frac{2\nu_n}{\pi}}\frac{(1-\cos\theta)^2}{\sin^2(\theta-\pi)}[\nu_n\sin(\theta-\pi)\cos\nu_n(\theta-\pi)-\cos(\theta-\pi)\sin\nu_n(\theta-\pi)]. \tag{8}$$

For $\pi-\theta\equiv\beta\ll 1$, it follows that from Eq. (8)

$$g_{nl}(q)=-i\frac{4}{\beta^3}\sqrt{\frac{2\nu_n}{\pi}}[\sin\nu_n\beta-\nu_n\beta\cos\nu_n\beta]. \tag{9}$$

From Eq. (6) we obtain the expression for electron density in the momentum space

$$|g_{nl}(q)|^2q^2=\frac{\nu_n}{\pi}(1-\cos\theta)^2[1-(-1)^l\cos 2\nu_n(\theta-\pi)]. \tag{10}$$

As we see, it oscillates with a change in q. If the amplitude of electron forward scattering $f_q(0)$ has a sufficiently narrow peak for $q=q_r$, the second term in Eq. (10) can give a positive or negative contribution (depending on ν_n) to the integrals in Eqs. (3) and (4).

We will investigate the scattering by a quasi-discrete level. For an energy of the incident electron E which is close to the energy of the quasi-discrete level ε_r, the amplitude of L scattering can be written in the form[13]

$$f_L^R=-\frac{\gamma}{\sqrt{2}(E-\varepsilon_r+i\gamma\sqrt{E})},\quad \gamma=\frac{\Gamma}{2\sqrt{\varepsilon_r}}, \tag{11}$$

where Γ is the resonance width in which we replaced E by ε_r, since due to large atom polarizability, Eq. (11) is valid only for $E\approx\varepsilon_r$.

The contribution to the shift $\Delta_{Ls}^R(n,l)$ and the width $\gamma_{Ls}^R(n,l)$ on account of scattering by the L-quasi-discrete level is obtained by substituting Eqs. (10) and (11) into Eqs. (3) and (4) and integrating with respect to θ in accordance with Eq. (7). Finally we obtain

$$\Delta_{Ls}^R(n,l)=NC(S_T)(2L+1)\nu_n\sqrt{b}(I_1-(-1)^lI_3), \tag{12}$$

$$\gamma_{Ls}^R(n,l)=2NC(S_T)(2L+1)\nu_nb(I_3-(-1)^lI_4), \tag{13}$$

where $C(S_T)$ is a relative number of states with total spin S_T at which the resonance occurs.

The integrals I_2 and I_4 were calculated in Ref. 12 with the aid of the substitution $z=\exp(i\theta)$. The integral I_1 is calculated analogously and I_3 by direct integration. As a result, we have

$$I_1=-2(2+a)\pi, \tag{14}$$

$$I_2=\frac{2\pi}{1-\sqrt{b}}\frac{(1+a)^2}{\sqrt{1-a^2}}\left(\frac{1-\sqrt{b}}{1+\sqrt{b}}\right)^{\nu_n}\sin 2\nu_n(\theta_r-\pi), \tag{15}$$

$$I_3=\frac{2\pi}{\sqrt{b}}\frac{(1+a)^2}{\sqrt{1-a^2}}+4\left[1-(a+1)\ln\frac{1+a}{1-a}\right], \tag{16}$$

$$I_4=\frac{2\pi}{\sqrt{b}}\frac{(1+a)^2}{\sqrt{1-a^2}}\left(\frac{1-\sqrt{b}}{1+\sqrt{b}}\right)^{\nu_n}\cos 2\nu_n(\theta_r-\pi). \tag{17}$$

Equations (15) and (17) were obtained for $b\ll 1$, where

$$b=\frac{\Gamma^2\nu_n^2}{q_r^2(1+\nu_n^2q_r^2)^2},\quad a=\frac{1-\nu_n^2q_r^2}{1+\nu_n^2q_r^2},\quad q_r=\sqrt{2\varepsilon_r} \tag{18}$$

and θ_r is determined by the expressions

$$\sin\theta_r=\frac{\sqrt{1-a^2-b}}{\sqrt{1-b}},\quad \cos\theta_r=\frac{-a}{\sqrt{1-b}}. \tag{19}$$

The substitution of Eqs. (14)–(17) into Eqs. (12) and (13) gives

$$\Delta_{Ls}^R(n,l)=-2\pi NC(S_T)(2L+1)\Gamma\nu_n^2\frac{3+\nu_n^2q_r^2}{q_r(1+\nu_n^2q_r^2)^3}+(-1)^{l+1}4\pi NC(S_T)A_L\sin X(\nu_n), \tag{20}$$

$$\gamma_{Ls}^R(n,l)=8\pi NC(S_T)\frac{\Gamma\nu_n}{q_r^2(1+\nu_n^2q_r^2)^2}+8\left[1+\frac{4}{1+\nu_n^2q_r^2}\ln(\nu_nq_r)\right]\times\frac{NC(S_T)(2L+1)\Gamma^2\nu_n^3}{q_r^2(1+\nu_n^2q_r^2)^2}+(-1)^{l+1}8\pi C(S_T)A_L\cos X(\nu_n), \tag{21}$$

$$A_L=\frac{(2L+1)\Gamma\nu_n}{q_r^2(1+\nu_n^2q_r^2)^2}\left(\frac{1+\nu_n^2q_r^2-\Gamma\nu_nq_r^{-1}}{1+\nu_n^2q_r^2+\Gamma\nu_nq_r^{-1}}\right)^{\nu_n}, \tag{22}$$

$$X(\nu_n)=2\nu_n(\theta-\pi). \tag{23}$$

As we see, the shift and the width have oscillating components. It is not difficult to establish that the oscillation amplitude is a maximum for

$$\Gamma=\frac{1+\nu_n^2q_r^2}{2\nu_n^2}q_r,\quad A_{L,\max}\approx\frac{2L+1}{2e(1+\nu_n^2q_r^2)\nu_nq_r}. \tag{24}$$

The oscillation period is determined by the resonance energy ε_r and depends on ν_n.

LIMITS OF APPLICABILITY

The conditions of statistical independence of the broadening due to the scattering and polarization effects and the limits of applicability of Eqs. (5) are given in Ref. 7. They have the form

$$\chi_i=\rho_i^3N=\frac{\pi}{4}\frac{aN}{V}\ll 1,\quad \rho_i=\left(\frac{\pi}{4}\frac{a}{V}\right)^{1/3}\ll\nu_n^2. \tag{25}$$

It is necessary to investigate in more detail the limits of applicability of Eqs. (20)–(22). Equations (3) and (4) were obtained using the impact approximation.[7,14] Equations (3) and (4) are analogous to the momentum approximation[15] in collisional theory. The basic condition of applicability of both the impact approximation in the theory of broadening of spectral lines[14] and the momentum approximation in collisional theory[15] is the minuteness of the duration of a collision $\Delta\tau$ as compared with the average time between collisions τ. In the case of scattering by a quasi-discrete level, the duration of a

collision is determined by the level width[16]: $\Delta\tau \approx \Gamma^{-1}$. The time between collisions τ is related to the width of the spectral line γ and for $\Gamma \ll (2\nu_n^2)^{-1}$, according to Eq. (21), it can be written that

$$\tau = \left[8\pi NC(S_T)(2L+1)\frac{\Gamma\nu_n}{q_r^2(1+\nu_n^2q_r^2)^2}\right]^{-1}. \quad (26)$$

The condition of applicability of Eqs. (20)–(22) acquires the form

$$\frac{\Delta\tau}{\tau} \approx \frac{8\pi NC(S_T)(2L+1)\nu_n}{q_r^2(1+\nu_n^2q_r^2)^2} \ll 1. \quad (27)$$

APPLICATION OF ALKALI METALS

Mazing and Serapinas[8] observed the oscillations of the width and shift of highly excited np levels of Cs in cesium vapor with increasing n in the 18–30 range. If one assumes that the width oscillates as $\cos\varphi(n)$, where $\varphi(n)$ is a monotonically increasing function of n, the shift oscillates as $-\sin\varphi(n)$. We should note that Ref. 8 gives $-\Delta(n)$ (red shift). In the impact approximation the broadening of a spectral line can be caused by both elastic and inelastic collisions.[14] The appearance of inelastic processes leads to an increase in the width and a decrease in the shift, i.e., the oscillations of the width and shift, determined by inelastic processes, must be of the opposite phase. In this way, it is natural to assume that the oscillations are caused by the presence of resonance in the scattering of electrons by the Cs atom and are described by Eqs. (20) and (21). Using Eq. (19), we can write Eq. (23) for $b \ll 1$ in the form

$$X(\nu_n) = -4\nu_n \operatorname{arctg}(\nu_n q_r) = -4\nu_n\left(\nu_n q_r - \frac{\nu_n^3 q_r^3}{3} \pm \ldots\right). \quad (28)$$

Since the oscillations are large, therefore, according to Eq. (24), it follows that $\nu_n q_r \ll 1$. The oscillating parts of the shift and width, according to Eqs. (20) and (21), acquire the form

$$\Delta_{L_s}^{R,\,\mathrm{osc}}(n, l) = (-1)^l 4\pi NC(S_T) A_L \sin(4\nu_n^2 q_r), \quad (29)$$

$$\gamma_{L_s}^{R,\,\mathrm{osc}}(n, l) = (-1)^{l+1} 8\pi NC(S_T) A_L \cos(4\nu_n^2 q_r). \quad (30)$$

We separate the oscillating components from the experimentally measured[8] shift and width. From the oscillation period, it is not difficult to establish q_r. The quantum defect for Cs is $\delta = 3.55$, i.e., $\nu_n = n - 3.55$. The value $q_r \approx 7.4 \times 10^{-3}$ corresponds best to the experiment. The oscillation amplitudes[8] are at a maximum at $n \approx 22$ and reach 0.17 cm^{-1} for the shift and 0.30 cm^{-1} for the width. The density of Cs is $N = 1.3 \times 10^{17}$ cm^{-3}. If one assumes that in the triplet s-scattering a resonance occurs, the maximum possible oscillation amplitudes are approximately three times smaller than the experimental ones. Consequently, it is natural to assume that a resonance exists in the triplet p-scattering of the electron by the Cs atom at an energy $\varepsilon_r \simeq 7.5 \times 10^{-4}$ eV, and the resonance width, according to Eq. (22), is $\Gamma \approx 3 \times 10^{-4}$ eV. We should note that, according to the decrement of the oscillation attenuation, the ^3P resonance corresponds best to the experiment.[8] The substitution of $q_r = 7.4 \times 10^{-3}$ in Eq. (27) for $\nu_n = 18$ gives $\Delta\tau/\tau = 0.35$, which is at the limit of applicability of the criterion (27). The other criteria of applicability of the theory, namely, $b \ll 1$ and $\Gamma \ll (2\nu_n^2)^{-1}$, are fulfilled by a large margin. Since in our case $\nu_n q_r \ll 1$, the basic contribution to the integrals (15)–(18) is provided by δ, which are close to π. Therefore, it is more proper to apply Eq. (8), but then we will not succeed in obtaining analytic expressions for the shift and broadening. However, using Eq. (9) it is easy to refine the positions of the oscillation extrema. The expression for electron density (10) crosses the maxima, minima, or medium values at $\varphi_k \equiv \nu_n(\pi - \vartheta) = k\pi/4$, and for electron density defined by Eq. (9), at $\varphi_k' = \varphi_k - \delta_k$, where δ_k is a correction determined by numerical methods. For large k Eq. (8) transforms into Eq. (6) and, consequently, $\delta_k \approx \varphi_k^{-1}$. For small k, δ_k and φ_k' are given in Table I.

TABLE I.

	k									
	3	4	5	6	7	8	9	10	11	12
δ_k	0.67	0.40	0.25	0.22	0.20	0.17	0.13	0.12	0.11	0.10
φ_k'	1.69	2.74	4.18	4.49	5.30	6.11	6.94	7.73	8.53	9.32
$-\Delta,\ \gamma$	$-\Delta_{\min}$	$\gamma_{\max}$	$-\Delta_{\max}$	$\gamma_{\min}$	$-\Delta_{\min}$	$\gamma_{\max}$	$-\Delta_{\max}$	$\gamma_{\min}$	$-\Delta_{\min}$	$\gamma_{\max}$

Figure 1 gives a comparison of the theoretically calculated [using Eqs. (29) and (30)] and experimental oscillating components of the shift and width. The oscillation phases were refined with the aid of Table I. Figure 2 compares the total experimental widths and shifts with the theoretical ones calculated by Eq. (2), when the polarization components are calculated by Eq. (5), the resonance components by Eqs. (20)–(22), and a term is added to the shift which corresponds to the potential s-scattering and is taken from Ref. 8. Let us note that for $n \gtrsim 40$, condition (27) is violated. In view of the satisfactory agreement of theory with experiment, the conclusion can be made that the assumed ^3P resonance of width $\Gamma \approx 3 \times 10^{-4}$ eV in the scattering of the electron with an energy $\varepsilon_r \approx 7.5 \times 10^{-4}$ eV by the Cs atom allows us to explain both the nonmonotonic behavior of the width and shift of spectral lines at a series limit and the large widths. The existence of such a resonance is not unexpected since in Ref. 10 similar resonances were calculated for lighter alkali metals: Li, Na, and K. They occur at energies of 6.0×10^{-2}, 8.3×10^{-2}, and 2.4×10^{-3} eV and have widths of 5.7×10^{-2}, 8.5×10^{-2}, and 5.8×10^{-4} eV, respectively.

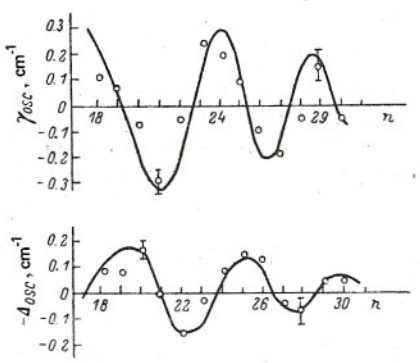

FIG. 1. Oscillating part of the width γ_{osc} and shift Δ_{osc} of the $6s$–np lines of Cs as a function of n. Circles—experimental results[8] for $N = 1.3 \times 10^{17}$ cm^{-3}, $T = 366$ °C; curve—data calculated by Eqs. (29)–(30) for $L = 1$, $C(S_T) = 3/4$, $\varepsilon_r = 7.5 \times 10^{-4}$ eV, $\Gamma = 3 \times 10^{-4}$ eV with corrections indicated in the text.

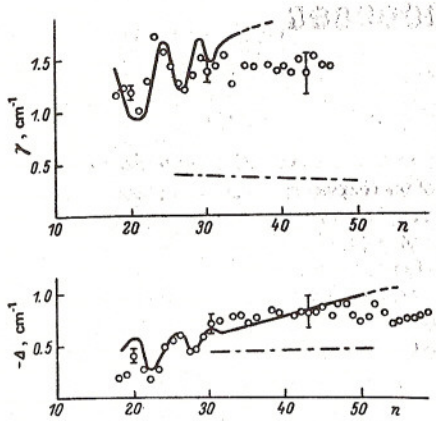

FIG. 2. Width γ and shift Δ of the $6s$–np lines of Cs as a function of n. Circles—experimental results[8]; curve—calculation, for explanation see the text; parameters are the same as in Fig. 1.

In Ref. 8, the widths and shifts of potassium lines in potassium vapor ($N = 2.6 \times 10^{17}$ cm^{-1}) were also measured. For $n = 30$–40, the experimental widths are $\gamma_{exp} \approx 2.7$ cm^{-2} and shifts $\Delta_{exp} \approx 1.05$ cm^{-1}. Within the limits of experimental accuracy, oscillations were not observed. The substitution of theoretical[10] parameters of the ^3P resonance for potassium in Eqs. (20)–(22) for $n \approx 35$ give $\gamma^R \approx 1.4$ cm^{-1} and $\Delta^R \approx 0.5$ cm^{-1}. These values, together with the width and shift due to polarizability and potential scattering [$\gamma_T \approx 0.7$ cm^{-2} and $\Delta_T \approx 0.5$ cm^{-2} (Ref. 8)], completely explain the experimentally measured shifts and account for more than 70% of the experimental widths. Due to a comparatively high energy of the ^3P resonance for potassium, the oscillation amplitude of linewidths for $n = 20$–30 is ~0.3 cm^{-1}. We should note that the oscillation amplitude (22) is very sensitive to the resonance width Γ. If actually the resonance in electron scattering by the potassium atom is by several percent wider than the one theoretically calculated in Ref. 10, the oscillations in the width and shift are within the limits of experimental errors.

Let us formulate the basic results of the present work. From experimental data in Ref. 8, it follows that in the scattering of electrons by the Cs atom at an energy $\varepsilon_r \approx 7.5 \times 10^{-4}$ eV, the ^3P resonance having a width $\Gamma \approx 3 \times 10^{-3}$ eV occurs. This allows us to explain simultaneously the large widths of spectral lines at a series limit as well as the oscillating structures of the width and shift for $n = 18$–30. The presence of analogous resonance in the case of potassium explains the large widths of potassium lines. However, due to a relatively large energy of the resonance, the oscillations are small. The theory of Alekseev and Sobelman[7] remains correct also in the case of perturbation by alkali-metal atoms if the amplitude of electron scattering by the perturbing atoms is calculated with sufficient accuracy. The investigation of the broadening of highly excited levels in a foreign gas can be an effective means for the search of resonances in the scattering of very slow electrons by atoms and molecules, when other experimental methods become unsuitable.

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