SOVIET PHYSICS JETP VOLUME 22, NUMBER 4 APRIL, 1966

A SPECTROSCOPIC METHOD FOR THE INVESTIGATION OF ELASTIC SCATTERING OF SLOW ELECTRONS

V. A. ALEKSEEV and I. I. SOBEL'MAN

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor May 7, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 1274-1283 (October, 1965)

A relation is established between the shift Δ and width γ of a spectral line near the edge of the series and the amplitude for the scattering of electrons by perturbing atoms. The contribution of an arbitrary number of partial waves to the scattering is considered, with exchange interaction taken into account. An examination of the broadening of the spectral lines of Na by argon shows that the calculated phase shifts can be checked against the experimental values of Δ and γ.

1. Fermi has shown[1] that the effective cross section for the elastic scattering of various slow electrons by neutral perturbing particles can be determined from the line shift caused by these particles in the absorption spectrum of alkaline metal atoms[1)] (see also[2]).

According to Fermi, the shift of the absorption line corresponding to the transition from the ground level to a level with a large principal quantum number n is due to two effects—scattering of the atomic electron in the state n by the perturbing particles, and polarization of the perturbing particles situated inside the atomic volume $(a_0 n^2)^3$, where a_0 is the atomic unit of length. Fermi obtained[1] for the line shift Δ_{sc} due to the scattering effect the expression

$$\Delta_{sc} = \pm \frac{\hbar}{m} (\pi\sigma_0)^{1/2} N, \tag{1}$$

where m is the electron mass, σ_0 the effective cross section for elastic scattering of an electron by a perturbing atom (or molecule) in the limiting case of very low velocities, and N the concentration of the perturbing atoms.

The contribution Δ_p of the polarization effect to the line shift has according to[1], an order of magnitude $-10\,\alpha e^2 N^{4/3}/\hbar$, where α is the polarizability of the perturbing atoms and e the electron charge. At relatively low pressure the polarization shift is small and therefore the cross section σ_0 can be determined from measurements of the shift for the higher terms of the absorption series. Thus, the values of σ_0 were obtained for the atoms He, Ne, Ar, Kr, and Xe from the shift of the absorption lines of Cs in a noble-gas atmosphere[3]. The same method was used to investigate several other gases[3,4].

The influence of the surrounding particles on the absorption spectrum near the edge of the series, that is, at large values of n, was later considered by Firsov[2,5], who studied the effects of the polarization and of the conditions for the applicability of formula (1) in much greater detail than in[1]. He showed that formula (1) is valid only if the most probable value of the electron velocity in the state n is so small that the main contribution to the cross section is made by s-scattering, the corresponding scattering phase shift being much smaller than unity[2)].

In some cases it is very difficult to satisfy these conditions. Recently, in connection with many applications, the problem of determining the cross sections for elastic scattering of slow electrons by alkaline-element atoms has become quite timely. In this case, even at very low electron energies, lower than 0.01 eV, there are no grounds for neglecting the contribution made to scattering by waves with $l \neq 0$.

We investigate in this paper the connection of the shift and width of the spectral lines near the edge of the series with the amplitude for the scattering of electrons by the perturbing atoms. We

---

[1)] The alkaline elements are most convenient because their absorption spectra are located in the visible and in the near-ultraviolet regions of the spectrum.

[2)] More accurately, it is necessary that the quantities $\delta_0 - p\pi$ (p = 0, 1, 2, ...) be small. The scattering phase δ_l is defined throughout as that part of the phase which remains in the interval $(-\pi/2, \pi/2)$ after subtracting $p\pi$.

include the contribution made to the scattering by an arbitrary number of partial waves, with account taken of the exchange interaction, and without any limitation whatever on the magnitude of the scattering phases δ_l.

2. Let us consider the influence of the surrounding particles on the absorption spectrum near the edge of the series, assuming that the impact-broadening theory is applicable. We assume also that we can neglect the contribution made to the broadening by the inelastic collisions. The conditions for the applicability of such an approximation will be indicated below.

In the general case of a transition between degenerate levels, the distribution $I(\omega)$ of the intensity in the line is given by the expression

$$I(\omega)=\sum_{\beta} I_\beta \frac{\gamma_\beta/2\pi}{(\omega-\omega_0+\Delta_\beta)^2+(\gamma_\beta/2)^2}, \tag{2}$$

where I_β, γ_β, and Δ_β are the intensity, width, and shift of the maximum of each of the line components;

$$\gamma_\beta = 2N\langle v\sigma_\beta'\rangle, \qquad \Delta_\beta = N\langle v\sigma_\beta''\rangle, \tag{3}$$

N and v are the concentration and the velocity of the perturbing particles, σ_β' and σ_β'' are the effective cross sections of the width and of the shift. The angle brackets denote averaging over the velocities and over the orientation in the space of the vector **v** and of the angular momentum of the perturbing atom.

The line broadening corresponding to the transition from the ground state to a state with large value of n is determined almost entirely by the perturbation of the final strongly-excited level. In this case the cross sections σ_β' and σ_β'' can be expressed in terms of the forward amplitude f(0) for scattering of the perturbing particle by the atom in a state corresponding to the considered line component β. From formulas (37.79), (37.80), and (41.15) of[8] it follows that

$$\sigma_\beta' = \frac{2\pi}{K}\,\mathrm{Im}\, f_\beta(0), \qquad \sigma_\beta'' = \frac{2\pi}{K}\,\mathrm{Re}\, f_\beta(0), \tag{4}$$

where $K = Mv/\hbar$ is the wave vector of the perturbing atom, and M is its mass.

At first, to simplify the reasoning, we shall disregard the dependence of the scattering on the spin momenta—this will be done later. The forward scattering amplitude $f_\beta(0)$ is given by the expression

$$f_\beta(0) = -\frac{M}{2\pi\hbar^2}\langle \varphi_\alpha e^{i\mathbf{K}\mathbf{R}}\psi_\beta(\mathbf{r})\,|\,U\,|\,\Psi_{\alpha\mathbf{K},\beta}\rangle, \tag{5}$$

where **R** is the distance to the perturbing atom, φ_α the electronic wave function of the perturbing atom, ψ_β the wave function of the valence electron of the alkaline atom, U the interaction between the atoms, and $\Psi_{\alpha\mathbf{K},\beta}$ the exact wave function of the system, satisfying the usual boundary conditions of the scattering problem. The function $\Psi_{\alpha\mathbf{K},\beta}$ is the eigenfunction of the Hamiltonian

$$H = H_0 + \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + U, \tag{6}$$

where H_0 is the Hamiltonian of the perturbing atom, **P** the momentum of its nucleus, and $\mathbf{p}^2/2m + V(\mathbf{r})$ the Hamiltonian of the valence electron in the field of the atomic remainder. For sufficiently large values of n, the average distance of the valence electron from the nucleus is of the order of $a_0 n^2$ and is so large that the perturbing particle either interacts with the electron and does not interact with the atomic remainder, or, to the contrary, interacts only with the atomic remainder[3)]. In calculating the shift due to the scattering it is obviously necessary to consider only the interactions of the first type. Interactions with the atomic remainder make a contribution to the polarization shift. We must therefore take U to mean the interaction between the valence electron and the traveling atom.

Let us expand the function $\psi_\beta(\mathbf{r})$ in plane waves, that is, in the eigenfunctions of the Hamiltonian $\mathbf{p}^2/2m$:

$$\psi_\beta(\mathbf{r}) = (2\pi)^{-3/2}\int G(\beta\,|\,\mathbf{q})\, e^{i\mathbf{q}\mathbf{r}} d\mathbf{q}. \tag{7}$$

We expand also the function $\Psi_{\alpha\mathbf{K},\beta}$ in the eigenfunctions $\Phi_{\alpha'\mathbf{K}',\mathbf{q}}$ of the Hamiltonian (6) without the potential $V(\mathbf{r})$. The interaction U is taken into account exactly in the function $\Phi_{\alpha'\mathbf{K}',\mathbf{q}'}$. The expansion of functions $\Psi_{\alpha\mathbf{K},\beta}$ in terms of the functions $\Phi_{\alpha'\mathbf{K}',\mathbf{q}'}$ is written in the form

$$\Psi_{\alpha\mathbf{K},\beta} = (2\pi)^{-3/2}\int G(\beta\,|\,\mathbf{q}')\,\Phi_{\alpha\mathbf{K},\mathbf{q}'}\, d\mathbf{q}'. \tag{8}$$

Such an approximation is equivalent to the impulse approximation in the theory of nuclear collisions (see, for example,[6]). In its physical meaning it is equivalent to the approximation used by Fermi and Firsov[1,2,5].

Substituting (7) and (8) in (5), we obtain

$$f_\beta(0) = -\frac{M}{2\pi\hbar^2}(2\pi)^{-3}\int G^*(\beta\,|\,\mathbf{q})\, G(\beta\,|\,\mathbf{q}') \times \langle \varphi_\alpha e^{i\mathbf{K}\mathbf{R}+i\mathbf{q}\mathbf{r}}\,|\,U\,|\,\Phi_{\alpha\mathbf{K},\mathbf{q}'}\rangle\, d\mathbf{q}\, d\mathbf{q}'. \tag{9}$$

[3)] It is assumed that the perturbation is produced by neutral and non-hydrogenlike atoms.

If we go over from variables **R** and **r** to the variables $\mathbf{R}' = (M\mathbf{R} + m\mathbf{r})(M + m)^{-1}$ (the coordinate of the c.m.s. of the system of the perturbing atom plus electron) and $\boldsymbol{\rho} = \mathbf{R} - \mathbf{r}$, then

$$\langle \varphi_\alpha e^{i\mathbf{KR}+i\mathbf{qr}} | U | \Phi_{\alpha\mathbf{K},\mathbf{q}'}\rangle = (2\pi)^3 \langle \varphi_\alpha e^{i\boldsymbol{\varkappa}\boldsymbol{\rho}} | U(\boldsymbol{\rho}) | \Phi_{\alpha\boldsymbol{\varkappa}}\rangle \,\delta(\mathbf{q}-\mathbf{q}'),$$

$$\boldsymbol{\varkappa} = \frac{M}{m+M}\mathbf{q} - \frac{m}{M+m}\mathbf{K}. \tag{10}$$

Since the electron momentum $\hbar q$ is of order of magnitude $\hbar q_0/n$ in the state with principal quantum number n ($\hbar q_0 = p_0$ is the atomic momentum unit), it is easy to show that at temperatures (300—700)°K (the usual experimental conditions) $q \sim 20 n^{-1} K\sqrt{m/M}$. Consequently, for all the values of n of practical interest, which certainly do not exceed n = 100, we have $q \gg mK/M$ and $\boldsymbol{\kappa} \approx \mathbf{q}$. Thus,

$$f_\beta(0) = -\frac{M}{2\pi\hbar^2}\int |G(\beta|\mathbf{q})|^2 \langle \varphi_\alpha e^{i\mathbf{q}\boldsymbol{\rho}} | U(\boldsymbol{\rho}) | \Phi_{\alpha\mathbf{q}}\rangle \, d\mathbf{q}. \tag{11}$$

We can express the forward scattering amplitude $f_q^{\mathrm{el}}(0)$ of a free electron with momentum $\hbar q$ by the perturbing atom in terms of the same matrix element which enters in the right side of (11):

$$f_q^{\mathrm{e}}(0) = -\frac{m}{2\pi\hbar^2}\langle \varphi_\alpha e^{i\mathbf{q}\boldsymbol{\rho}} | U(\boldsymbol{\rho}) | \Phi_{\alpha\mathbf{q}}\rangle. \tag{12}$$

The quantity $f_q^{\mathrm{el}}(0)$ obviously depends only on the absolute value of the electron momentum $\hbar q$. Using (3) and (4), we obtain

$$v(\sigma_\beta'' + i\sigma_\beta') = \frac{2\pi\hbar}{m}\int |G(\beta|\mathbf{q})|^2 f_q^{\mathrm{el}}(0)\, d\mathbf{q}. \tag{13}$$

The index β is specified in this case by the quantum numbers of the valence electron. Therefore, (see, for example, [7])

$$G(\beta|\mathbf{q}) = G_{nl}(q) Y_{lm}(\theta_q, \varphi_q). \tag{14}$$

Integration over the angles θ_q and φ_q leaves in the right side of (13) the integral with respect to q, which contains the product of $f_q^{\mathrm{el}}(0)$ and the distribution function.

$$W(q) = q^2 |G_{nl}(q)|^2, \qquad \int W(q)\, dq = 1. \tag{15}$$

This integral does not depend on the quantum number m; consequently the widths and the shifts of all m → m′ components of the line are identical in this case. Therefore the scattering effect leads to a line broadening described by the dispersion formula with width γ_{sc} and shift of the maximum Δ_{sc}, where in accordance with (3) and (4)

$$\gamma_{\mathrm{sc}} = 2N\frac{2\pi\hbar}{m}\int \overline{[\operatorname{Im} f_q^{\mathrm{el}}(0)]}\, W(q)\, dq, \tag{16}$$

$$\Delta_{\mathrm{sc}} = N\frac{2\pi\hbar}{m}\int \overline{[\operatorname{Re} f_q^{\mathrm{el}}(0)]}\, W(q)\, dq. \tag{17}$$

The superior bar denotes averaging over the orientation of the momentum of the perturbing atom. Expressing $f_q^{\mathrm{el}}(0)$ in terms of the phases for the scattering of the electron by the perturbing atom δ_l [8], we obtain also

$$\gamma_{\mathrm{sc}} = N\frac{\hbar}{m}\int \left[\frac{4\pi}{q}\sum_l (2l+1)\sin^2\delta_l\right] W(q)\, dq$$
$$= N\frac{\hbar}{m}\int q\sigma(q) W(q)\, dq, \tag{18}$$

$$\Delta_{\mathrm{sc}} = N\frac{\hbar}{m}\int \left[\frac{\pi}{q}\sum_l (2l+1)\sin 2\delta_l\right] W(q)\, dq. \tag{19}$$

Here $\sigma(q)$ is the effective cross section for elastic scattering of an electron with momentum $\hbar q$ by the perturbing atom. In the same approximation as used above, we can repeat the derivation of formulas (16)—(19) but with exchange interaction taken into account. If the spin of the perturbing atom is S, then the new spin of the system S_T can assume two values, $S_T = S + 1/2$ and $S_T = S - 1/2$ (with $S \neq 0$). The relative number of collisions with given value of the total spin S_T is $C(S_T) = (2S_T + 1)/2(2S + 1)$. Accordingly, in formulas (16)—(19), when account is taken of the exchange interaction, we must make the substitution

$$f_q^{\mathrm{el}}(0) \to \sum_{S_T} C(S_T) f_{qS_T}^{\mathrm{el}}(0), \tag{20}$$

$$\sin^2\delta_l \to \sum_{S_T} C(S_T)\sin^2\delta_{lS_T}, \tag{21}$$

$$\sin 2\delta_l \to \sum_{S_T} C(S_T)\sin 2\delta_{lS_T}, \tag{22}$$

where δ_{lS_T} are the scattering phase shifts, calculated for the state of the system with specified value of the total spin S_T, with exchange taken into account.

States with large values of the principal quantum number n are hydrogenlike. We can therefore use for $G(\beta|\mathbf{q})$ the well known expressions for hydrogen functions in the momentum representation in terms of Gegenbauer polynomials [7]. For the transitions of interest to us, ^2S—^2P (the alkaline-atom absorption series), we obtain

$$W(q) = \frac{n}{2\pi(n^2-1)}\left(\frac{1}{nqa_0}\right)^2 [(n+1)\sin(n-1)\varphi$$
$$-(n-1)\sin(n+1)\varphi]^2 a_0, \tag{23}$$

$$\cos\varphi = (n^2q^2a_0^2 - 1)/(n^2q^2a_0^2 + 1). \tag{24}$$

The function W(q) has n maxima, of which n/2 are located in the region $0 < q < (na_0)^{-1}$. In this region the envelope behaves approximately like $(1 + n^2q^2a_0^2)^{-2}$. When $q \gg (na_0)^{-1}$, W(q) decreases monotonically:

$$W(q) \approx \frac{2^7}{3} \frac{(n^2 - 1) n^3}{\pi} \left(\frac{1}{nqa_0}\right)^8. \tag{25}$$

Thus, the main contribution to the integral with respect to q in (16)—(19) is made by the region $0 < q < (na_0)^{-1}$.

If n is so large that the principal role in this region is played by s-scattering and if in addition $q^{-1} \sin 2\delta_0$ differs little from its limiting value

$$\lim_{q \to 0} \left(\frac{1}{q} \sin 2\delta_0\right) = \frac{\delta_0}{|\delta_0|} \sqrt{\frac{\sigma_0}{\pi}}, \tag{26}$$

then, by taking this quantity outside the integral sign in (19), we obtain

$$\Delta_p = \frac{\hbar}{m} \sqrt{\pi\sigma_0} \frac{\delta_0}{|\delta_0|} N, \tag{27}$$

which coincides with (1).

Inasmuch as $q\sigma(q) \to 0$ when $q \to 0$, we get $\gamma_{sc} \ll \Delta_{sc}$ in the region where (1) and (27) are valid. Outside this region, in accordance with (18) and (19), γ_{sc} and Δ_{sc} have in general the same order of magnitude.

Let us ascertain now the conditions for the applicability of the approximation used above when considering the scattering effect.

The impact approximation in the theory of broadening of spectral lines is applicable in those cases when the duration $\Delta\tau$ of the collisions that make the greatest contribution to the broadening is small compared with the average time between collisions. Since the only interactions responsible for the broadening due to the scattering effect are those between the perturbing particles and the valence electron, which at large distances are of the form $U(\rho) \sim \alpha e^2 \rho^{-4}/2$, we must set $\Delta\tau$ equal to ρ_e/v_e, where

$$\rho_e = \left(\frac{\pi}{4} \alpha \frac{e^2}{\hbar v_e}\right)^{1/3} \tag{28}$$

is the effective radius of interaction between the electron and the neutral perturbing particle[8], $v_e = \hbar q/m \approx \hbar q_0/mn$. Therefore $\Delta\tau/\tau \approx \rho_e^3 N \equiv \chi_e$, and the condition $\Delta\tau/\tau \ll 1$ takes the form

$$\chi_e = \frac{\pi}{4} \alpha n N \ll 1. \tag{29}$$

In order for formulas (18) and (19) to be valid it is also necessary to satisfy the condition $\rho_e \ll a_0 n^2$, that is,

$$(\pi\alpha / 4a_0^3 n^5)^{1/3} \ll 1. \tag{30}$$

When this condition is satisfied in the region of interaction between the electron and the perturbing particle, the potential V(**r**) produced by the atomic remainder remains practically unchanged, thus justifying the use of the impulse approximation.

We have also implied tacitly above that the inelastic collisions make no appreciable contribution to the broadening. An elementary estimate of the value of energy ΔE transferred to an electron colliding with a neutral atom shows that ΔE does not exceed Ry/n^3 up to $n \leq 50$. This justifies the neglect of inelastic collisions.

3. Let us proceed to discuss the effect of polarization due to the interaction between the perturbing particles and the atomic remainder. This interaction leads to a shift in the frequency of the atomic oscillator[1,2,5]:

$$\varkappa(t) = -\frac{\alpha}{2\hbar} e^2 \sum_i [R_i(t)]^{-4}, \tag{31}$$

where R_i is the distance to the i-th perturbing particle. The most general analysis of the problem of the distribution of the intensity $I(\omega)$ in the spectrum of such an oscillator, with allowance for the thermal motion, is contained in the paper by Anderson and Talman[9] (see also[5]). The results of this paper show that within the limits of the accuracy on which one can generally count in the framework of the model of (31), the contour of the line can be constructed from the results of the impact and statistical approximations[8].

If the dimensionless parameter is

$$\chi_i = \rho_i^3 N \equiv \left(\frac{\pi}{4} \alpha \frac{e^2}{\hbar V} N\right) \ll 1, \tag{32}$$

where V is the average velocity of the perturbing particles, then the central part of the line

$$|\omega - \omega_0| \ll \Omega = (2\hbar V^4 / \alpha e^2)^{1/3} \tag{33}$$

is described by a dispersion contour with width γ_p and shift Δ_p, defined by the formulas

$$\gamma_p = 11.4 (\alpha e^2 / 2\hbar)^{2/3} V^{1/3} N, \qquad \Delta_p = -\sqrt{3}\, \gamma_p / 2. \tag{34}$$

In the long-wave wing of the line ($(\omega - \omega_0) < 0$ and $|\omega - \omega_0| \gg \Omega$) the dispersion distribution is replaced by the statistical distribution

$$I(\omega) \approx \pi N (\alpha e^2 / 2\hbar)^{3/4} |(\omega - \omega_0)|^{-7/4}. \tag{35}$$

The statistical wing is located in the long-wave region because of the sign of the frequency shift in (31). The intermediate region $|\omega - \omega_0| \sim \Omega$ can be obtained by interpolating the dispersion contour and the distribution (35).

On the other hand, if $\chi_i \gg 1$, then the statistical approximation is applicable to the entire contour, and we have

$$I(\omega)=\frac{1}{\pi}\int\limits_0^\infty \exp(-Ng't^{3/4})\cos(\Delta\omega t+Ng''t^{3/4})\,dt,$$

$$g''+ig'=\frac{4\pi}{3}\left(\frac{\alpha e^2}{2\hbar}\right)^{3/4}\Gamma\left(\frac{1}{4}\right)e^{i\pi/8}, \tag{36}$$

when $(\omega-\omega_0)<0$ and $I(\omega)=0$ when $\Delta\omega=(\omega-\omega_0)>0$[4,5]. In the case (36) the width and the absolute magnitude of the shift are approximately equal to $10\,N^{4/3}\alpha e^2/\hbar$[5]. We note that the ratio of this quantity to $|\Delta_p|$ as given by (34) is $1.6\,\chi_i^{1/3}$.

When $|\omega-\omega_0|\gg 10\,N^{4/3}\alpha e^2/\hbar$, formula (36) goes over into (35). When $|\omega-\omega_0|\lesssim 10\,N^{4/3}\alpha e^2/\hbar$ we can obtain

$$I(\omega)\approx\sqrt{\frac{2}{\pi}}\frac{9}{16}\frac{\nu^{3/2}}{(\omega_0-\omega)^{5/2}}\exp\left[-\frac{1}{4}\left(\frac{3\nu}{4(\omega_0-\omega)}\right)^3\right],$$

$$\nu=\frac{\alpha e^2}{2\hbar}\left(\frac{4}{3}\pi\Gamma\left(\frac{1}{4}\right)N\right)^{4/3}. \tag{37}$$

When $\chi_i\ll 1$ the polarization broadening is determined almost entirely by the interaction of the atomic remainder with the particles which enter the sphere with radius $\rho_i=(\pi\alpha e^2/4\hbar V)^{1/3}$. On the other hand, when $\chi_i\gg 1$ the main contribution to the intensity distribution (36) in the region of the maximum is given by particles at a distance of the order of $\bar{R}=(3/4N)^{1/3}$. If condition (30) is satisfied, and also if

$$\chi_i\ll 1,\qquad \rho_i\ll a_0n^2 \tag{38}$$

or

$$\chi_i\gg 1,\qquad \bar{R}\ll a_0n^2, \tag{39}$$

then the broadening due to the scattering effect and the polarization effect are statistically independent[4)]. Therefore the resultant contour can be obtained by convolution of the intensity distributions from the scattering and polarization effects.

When $\chi_i\ll 1$ the central part of the line is described by a dispersion formula with width γ and shift of the maximum Δ, equal to

$$\gamma=\gamma_{sc}+\gamma_p,\quad \Delta=\Delta_{sc}+\Delta_p. \tag{40}$$

4. Let us estimate the values of the parameters χ_e and χ_i for typical experimental conditions. Inasmuch as $\chi_e\ll\chi_i$, the main interest is attached to the parameter χ_i.

For noble gases, the polarizability α is of the order of 1.5×10^{-24} cm^3. Therefore at velocities $V\approx 5\times10^4$ cm/sec, corresponding to the ordinary experimental conditions, $\chi_i\approx 0.5\times10^{-20}$ N. Thus, $\chi_i\ll 1$ up to pressures of the order of atmospheric. However, if the inequality $\chi_i\ll 1$ is satisfied with a small margin, then the polarization effect yields a noticeably asymmetrical distribution of the intensity, since $\gamma_p/\Omega=(22.8/\pi)\chi_i$. For example, when $\chi_i=5\times10^{-2}$ we get $\gamma_p/\Omega=0.35$ and consequently the statistical wing becomes noticeable at a distance of 2—3 line widths from the intensity maximum.

For the atoms of alkaline elements $\alpha\approx 50\times10^{-24}$ cm^3 and $\chi_i\approx 25\times10^{-20}$ N. In this case $\chi_i\ll 1$ up to $N\leq 5\times10^{17}$ cm^{-3}. Thus, in the pressure region of greatest interest for experiments $\chi_i\ll 1$ and the contribution of the polarization effect to the width and the shift of the line can be estimated from (34), while the total width and the shift can be calculated from (40).

Let us consider by way of an example the broadening and the shift of the higher-order terms of the principal series of absorption of Na in an atmosphere of Ar, experimentally investigated by Fuchtbauer and Schulz[10]. Under the experimental conditions the argon concentration was 2.7×10^{19} cm^{-3} at T = 762°K. The polarizability of the argon is $\alpha=1.63\times10^{24}$ cm^3. Therefore $\chi_i=0.12$, $\rho_i=1.64\times10^{-7}$ cm, and $\gamma_p/\Omega=0.87$. In accordance with (38), the experimental data can be compared with the formulas obtained above for $n^2>300$, that is, for $n\gtrsim 17$. Although the ratio γ_p/Ω is not small in this case, it follows from the concrete form of the polarization component of the contour that the statistical wing has practically no effect on the width or on the shift. We can therefore use formula (40) to calculate γ and Δ, and formulas (34) to calculate γ_p and Δ_p. In cm^{-1} units we have

$$\gamma_p=2.1,\qquad \Delta_p=1.82.$$

To determine γ_{sc} and Δ_{sc}, we calculated the scattering phase shifts δ_0, δ_1, and δ_2 for an electron scattered by an argon atom. The calculations took into account the exchange and the polarization of the argon atom by the electron in the adiabatic approximation. The wave functions of the argon atom were specified in the Slater approximation:

$$R_{nl}(r)=A_{nl}r^{\mu_{nl}}e^{-\beta_{nl}r}. \tag{41}$$

The potential of the atomic remainder can be calculated with the aid of functions (41) in analytic form only for integer and half-integer values of the parameters μ. In choosing μ and β for the states 1s, 2s, and 2p, we used the Slater prescription[11]:

$$\mu_{1s}=1,\qquad \mu_{2p}=\mu_{2s}=2,$$

$$\beta_{1s}=17.7,\qquad \beta_{2s}=\beta_{2p}=6.93.$$

[4)] Inasmuch as $\rho_i\gg\rho_e$, condition (30) is automatically ensured by the second inequality of (38).

Phases of elastic scattering by an argon atom

k	δ_0	δ_1	δ_2	δ_0
	$\beta_{3p} = 0.9$			$\beta_{3p} = 0.917$
0.01	3159^1	—	—	3155^1
0.02	3175^1	—	—	3167^1
0.03	3187^1	—	—	3176^1
0.04	3198^1	290^{-2}	460^{-3}	3183^1
0.08	3217^1	920^{-2}	200^{-2}	3191^1
0.12	3207^1	150^{-1}	470^{-2}	3174^1
0.16	3177^1	175^{-1}	850^{-2}	3139^1
0.20	3133^1	145^{-1}	136^{-1}	3092^1
0.24	3079^1	500^{-2}	203^{-1}	3036^1
0.28	3017^1	114^{-1}	293^{-1}	2973^1
0.32	2950^1	344^{-1}	409^{-1}	2906^1
0.36	2880^1	632^{-1}	561^{-1}	2836^1
0.40	2807^1	970^{-1}	101^0	2764^1

Remark. k – momentum of incident electron in atomic units. The numbers are in the form of decimal fractions and powers of 10, for example, $290^{-2} = 0.290 \times 10^{-2}$.

For the 3s and 3p states, the parameters μ and β were chosen by comparing (41) with the calculations of the wave functions of argon by the Hartree-Fock method[12,13]. Inasmuch as $\beta = \sqrt{\epsilon}$, where ϵ is the energy of the state and $\mu = \beta r_{\max}$ ($r_{\max}$ is the point corresponding to the maximum of the function (41)), we chose for μ the integer or half-integer closest to $\sqrt{\epsilon} r_{\max}$, and then determined $\beta = \mu / r_{\max}$. With such a choice of the parameters β and μ, the maxima of the function (41) and of the function obtained from the Hartree-Fock calculations occur at identical positions. We note that the functions of the 3s and 3p states given in[13] have a rather gently sloping maximum. Therefore there is some leeway in the determination of the parameters μ and β. The final criterion for the choice of the parameters was a comparison of the calculated elastic scattering cross sections with those obtained experimentally. The calculations were made with parameters $\mu_{3s} = 2$, $\mu_{3p} = 1$, $\beta_{3s} = 1.75$ and two values of the parameter $\beta_{3p} = 0.9$ and $\beta_{3p} = 0.917$. The scattering phase shifts δ_l were found by numerically solving the corresponding integro-differential equations. The polarization potential was assumed equal to $-\alpha e^2/2(r^2 + r_0^2)^2$, where α is the polarizability of the argon atom and $r_0 = 0.8 \times 10^{-8}$ cm. When the parameter β_{3p} is varied ($\beta_{3p} = 0.9$ and $\beta_{3p} = 0.917$), the phases δ_1 and δ_2 remain practically unchanged, so that the table lists the values δ_0, δ_1, and δ_2 for $\beta_{3p} = 0.9$, and the value of the phase δ_0 for the case $\beta_{3p} = 0.917$. The values of γ_{sc} and Δ_{sc} were obtained with the aid of formulas (18) and (22).

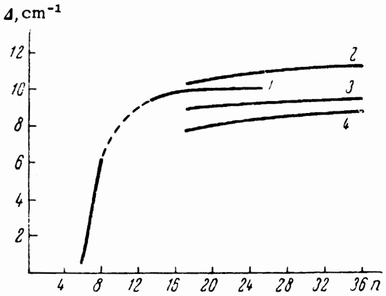

FIG. 1. Shift of the higher terms of the principal series of Na absorption in an atomosphere of argon: Curve 1 – experimental values [10]; 2 – calculation corresponding to $\beta_3 p = 0.9$; 3 – calculation corresponding to $\beta_3 p = 0.917$; 4 – calculation with account of one phase δ_0 corresponding to $\beta_3 p = 0.917$.

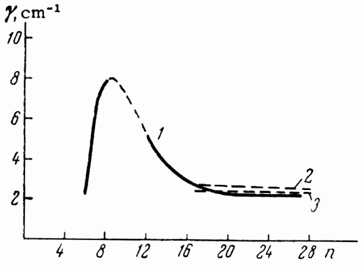

FIG. 2. Width of higher terms of principal series of absorption of Na in an argon atmosphere: 1 – experimental data of [10]; 2 – calculation corresponding to $\beta_3 p = 0.9$; 3 – calculation corresponding to $\beta_3 p = 0.917$.

Figures 1 and 2 show the results of the calculation of $\gamma = \gamma_{sc} + \gamma_p$ and $\Delta = \Delta_{sc} + \Delta_p$, and also the experimental results. We note that, in accordance with a remark made by Unsold[14], with reference to a private communication from Fuchtbauer, the experimental values of γ are reduced by 1.7 cm^{-1}.[5)]

Figure 3 shows a comparison of the experimental data of[15] with the effective cross section for the scattering of an electron by an argon atom, calculated in the same approximation as δ_{sc} and γ_{sc}.

It can be seen from Figs. 1 and 2 that the calculated values of Δ and γ agree well with the experimental ones, and that the calculation of the shift Δ is quite sensitive to the approximation employed. A relatively small change in the parameter β_{3p} changes Δ by approximately 20 per cent. Comparison of curves 2 and 3 shows that scattering with $l \neq 0$ (phases δ_1 and δ_2) plays a noticeable role in this case. Good agreement is obtained between calculation and experiment for the elastic-scattering cross section at the same values of the scattering phases (Fig. 3). Thus, comparison of the cal-

---

[5)] Unsold [14] does not indicate the cause of this additional broadening. Estimates of the broadening due to the interaction of Na atoms with other Na atoms give a value of γ which is considerably smaller than 1.7 cm^{-1}. Apparently the additional broadening is connected with self-absorption.

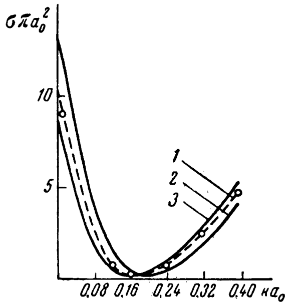

FIG. 3. Effective cross section for elastic scattering of electrons by an argon atom: Curve 1 – experimental data (point corresponding to the lowest energy of the incident electron – cross section for momentum transfer, the remaining points – total cross sections for elastic scattering of an electron by an argon atom); Curve 2 – calculation corresponding to $\beta_3 p = 0.9$; Curve 3 – calculation corresponding to $\beta_3 p = 0.917$.

culated and experimental values of γ and Δ makes it possible to monitor the quality of the scattering phase shift calculation.

We are grateful to L. A. Vaĭnshteĭn for an evaluation of the work.

---

[1] E. Fermi, Nuovo Cimento 11, 157 (1934).

[2] O. B. Firsov, JETP **21**, 627 (1951).

[3] H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, Cambridge, 1950, Ch. 3, Sec. 4.

[4] S. Chen and M. Takeo, Revs. Modern Phys. **29**, 20 (1957).

[5] O. B. Firsov, JETP **21**, 634 (1951).

[6] A. S. Davydov, Teoriya atomnogo yadra (Theory of Atomic Nucleus), Fizmatgiz, 1958.

[7] H. Bethe and E. Salpeter, Quantum Theory of One- and Two-electron Systems, Handb. Physik, v. 35, Springer, 1957.

[8] I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, 1963, Ch. 10.

[9] P. W. Anderson and J. D. Talman, Bell Telephone Laboratories, Murray Hill, New Jersey (1956).

[10] C. Fuchtbauer and P. Schulz, Z. Physik **97**, 699 (1935).

[11] J. Slater, Phys. Rev. **36**, 57 (1930).

[12] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).

[13] D. R. Hartree, Calculation of Atomic Structures (Russ. Transl.) IIL, 1960.

[14] A. Unsold, in coll. Sovremennye problemy astrofiziki i fiziki Solntsa (Modern Problems of Astrophysics and Physics of the Sun), IIL, 1951, p. 37.

[15] L. S. Frost and A. V. Phelps, Phys. Rev. **136**, 6A, A1538 (1964).

Translated by J. G. Adashko
164