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SCATTERING OF SLOW ELECTRONS ON ATOMS

Yu. V. MARTYNENKO, O. B. FIRSOV, and M. I. CHIBISOV[1)]

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Curves showing the velocity dependence of the total scattering cross section for electrons on atoms at energies $\lesssim 1$ eV are plotted using the atomic polarizability and one constant, which can be determined either from one point of the $\sigma(E)$ curve, or from the binding energy of the negative ion. The temperature dependence of the mean collision frequency of the electrons in the gas is determined.

In the present work we have obtained curves showing the dependence of the total scattering cross section for slow ($E \lesssim 1$ eV) electrons on atoms. In this energy region many atoms exhibit a nonmonotonic dependence of scattering cross section on energy (Ramsauer effect). This effect has been treated by many authors on the basis of scattering on various potentials.

We analyze scattering of the electron caused by the interaction, induced by the electron itself, with the field of the atomic dipole. This potential of the interaction is

$$U = -\alpha e^2 a^3 / 2r^4, \tag{1}$$

where α is the polarizability in atomic units while a is the Bohr radius. This potential is effective outside the atom. The results of calculations of the interaction energy of a point charge with a hydrogen atom in the second perturbation-theory approximation[1,2] differ from the potential in (1) by less than 25—35% even when $r \approx 2a$. The notion of a potential and wave function for a single isolated electron does not have meaning inside the atom in our scattering problem. However, when $E \sim 1$ eV the effect of the atom at small r can be taken into account in the boundary conditions imposed on the wave function at $r \to 0$; that is to say, instead of assigning a potential inside the atom we specify the boundary condition.

1. The Schrödinger equation for scattering on the potential described by (1) is

$$\varphi'' + \frac{2m}{\hbar^2}\left(E + \frac{\alpha e^2 a^3}{2r^4}\right)\varphi = 0, \tag{2}$$

where $\varphi(r) = rR(r)$ and $R(r)$ is the radial part of the wave function characterized by $l = 0$. Introducing the notation $x = r\alpha^{-1/4}\sqrt{k/a}$, $\beta^2 = ka\sqrt{\alpha}$ we have

$$\varphi'' + \beta^2(1 + 1/x^4)\varphi = 0. \tag{3}$$

When $x \gg 1$ we have $\varphi = A\sin(\beta x + \delta_0)$ (δ_0 is the zeroth scattering phase). The higher phases can be neglected if $U(p) \ll \hbar^2 k/2m$ where $p = \sqrt{l(l+1)}/k$ is the analog of the classical impact parameter.

The condition that the contribution due to p-scattering be small is $\beta \ll \sqrt{2}$ or $E \ll 54/\alpha$. This condition is especially stringent for atoms with high polarizability. Thus, in alkali metal vapors, in which $\alpha \sim 100$, we can only consider scattering at $E \sim 0.1$ eV. For example, in cesium at $E = 0.25$ eV we find $\sigma = 326 \times 10^{-16}$ cm^2[3] and $\Sigma_l (2l+1)\sin^2\delta_l = 1.73$; thus, when $E = 0.25$ eV we must at least include effects due to p-scattering.

We now note that Eq. (3) is invariant under the substitution $x = 1/\xi$, $\varphi = \psi/\xi$. Hence, when $x \ll 1$, $\xi \gg 1$

$$\psi = B\sin(\beta\xi + \gamma), \qquad \varphi = Bx\sin(\beta/x + \gamma). \tag{4}$$

Knowledge of the constant γ is equivalent to knowledge of the boundary condition at $r \to 0$. In practice the solution of Eq. (4) for φ applies for $(1.5-2)x_0 < x < 0.7$ or $(1.5-2)r_0 < r < 0.7\alpha^{1/4}\sqrt{a/k}$ where r_0 is the effective radius of the atom ($x_0 = r_0\alpha^{-1/4}\sqrt{k/a}$). This condition imposes the limitation $0.7\sqrt{a/k}\,\alpha^{1/4} > (1.5-2)r_0$ on the choice of atoms suitable for this analysis. The quantity γ can be given if either one point of the Ramsauer curve or the binding energy of the negative ion is known.

We now find the solutions of Eq. (3) for $x > 1$ and $x < 1$. Treating β^2/x^4 as a perturbation, as a first approximation we find: for $x < 1$

$$\varphi = Bx\left[\sin\left(\frac{\beta}{x} + \gamma\right) + \beta\int_{1/x}^{\infty}\sin\beta\left(\frac{1}{x} - \xi\right)\sin(\beta\xi + \gamma)\frac{d\xi}{\xi^4}\right], \tag{5}$$

[1)] M. I. Chibisov contributed the calculations in Sec. 2b.

or for x > 1

$$\varphi = A\left[\sin(\beta x + \delta_0) + \beta\int_x^\infty \sin\beta(x - x')\sin(\beta x' + \delta_0)\frac{dx'}{x'^4}\right]. \qquad (6)$$

If this approximation is to hold for x = 1 we must satisfy the condition

$$\beta\int_1^\infty \sin\beta(1 - x)\frac{dx}{x^4} \ll 1,$$

but

$$\beta\int_1^\infty \sin\beta(1 - x)\frac{dx}{x^4} = \frac{\beta^4}{6}\int_0^\infty \frac{e^{-\beta\xi}\xi^3 d\xi}{1 + \xi^2} \ll 1,$$

and furthermore

$$\frac{\beta^4}{6}\int_0^\infty \frac{e^{-\beta\xi}}{1 + \xi^2}\xi^3 d\xi < \frac{9\pi}{8}\beta e^{-3} \approx 0.18\,\beta.$$

Thus, the error is determined primarily by the contribution due to p-scattering, which has been neglected, rather than the error in the approximation.

Equating the logarithmic derivatives of the functions in (5) and (6) at x = 1, after some simple transformations we have

$$\operatorname{tg}\delta_0 = [A(\beta) + \operatorname{tg}\gamma]/[B(\beta)\operatorname{tg}\gamma - 1]. \qquad (7)^*$$

The values of the functions A and B are as follows:

$\beta =$	0.2	0.4	0.6	0.8	1	1.2	1.4
$A =$	—25.33	—6.865	—3.27	—1.91	—1.201	—0.748	—0.36
$B =$	—637.3	—45.47	—10.87	—4.29	—2.173	—1.225	—0.70

When $\beta < 0.2$, the functions A and B are

$$A = -3/\pi\beta^2 - 1.15/\beta, \qquad B = -3/\pi\beta^4 - 1.15/\beta^3.$$

To get more precise values for A and B when $\beta \gtrsim 1$ we find their asymptotic forms, using the quasi-classical approximation; the validity of this approximation requires $|(\hbar/p)(dp/dx)| \ll 1$, where $p = \hbar\beta\sqrt{1 + 1/x^4}$, i.e., $\beta \gg 1$. In this approximation the wave function is

$$\varphi = \left(1 + \frac{1}{x^4}\right)^{-1/4}\sin\left[\beta\int_1^x \sqrt{1 + \frac{1}{x^4}}\,dx + c\right]. \qquad (8)$$

When $x \ll 1$ the function in (8) must become $\varphi = x\sin(\beta/x + \gamma)$ and when $x \gg 1$ this function is $\varphi = \sin(\beta x + \delta_0)$; hence, $\delta_0 = -1.7\beta - \gamma + k\pi$ and

$$\begin{aligned} A &= \operatorname{tg} 1.7\beta \quad \text{for} \quad \beta > 1.8, \\ B &= -\operatorname{tg} 1.7\beta \quad \text{for} \quad \beta > 1.8. \end{aligned} \qquad (9)$$

We find the cross section from the expression

$$\sigma = \frac{4\pi}{k^2}\frac{\operatorname{tg}^2\delta_0}{1 + \operatorname{tg}^2\delta_0}. \qquad (10)$$

The cross section found in this way applies for scattering on spherically symmetric atoms with spin zero. The total scattering cross section for spherically symmetric atoms of spin ½ is σ $(\sigma_s + 3\sigma_a)$ where σ_s is determined by means of the symmetrized wave function and σ_a by means of the antisymmetrized wave function. In general we must assign two constants, γ_s and γ_a, for this case.

2. We now consider methods for determining γ from certain characteristic quantities.

A. When k → 0, we find from Eqs. (6) and (10)

$$\sigma = 4\pi a^2\alpha \operatorname{ctg}\gamma\,[1 - (0.51 + 2.10\operatorname{tg}\gamma)\,ka\sqrt{\alpha}]. \qquad (11)^*$$

Thus

$$\operatorname{ctg}\gamma = \pm(2a)^{-1}\sqrt{\sigma_0/\pi\alpha}, \qquad (12)$$

where σ_0 is the cross section for limitingly small energies. We note that the plus sign corresponds to a frequency shift toward the red transitions from higher levels of alkali metal atoms in foreign gases [4] while the minus sign corresponds to a shift toward the violet. Equation (12) can be used to determine γ from the known quantity σ_0. From Eq. (11) we have

$$\left.\frac{d\sigma}{dE}\right|_{E\to 0} = \begin{cases} +\infty & \operatorname{tg}\gamma < -0{,}242 \\ -\infty & \operatorname{tg}\gamma > -0{,}242 \end{cases}. \qquad (13)$$

The second possibility is realized in practice either in the case of very narrow resonance scattering or when $\tan\gamma > 0$, i.e., in atoms in which a Ramsauer effect is observed.

B. We now consider the possibility of determining γ from a given value of the discrete level of the electron-atom system. Physically γ depends on the behavior of the electron inside the atom, and is independent of the behavior of the wave function outside the atom. The quantity γ can thus be determined by considering the stable bound state of the electron with the atom. In this case we are given the behavior of the wave function for $r \to \infty$ ($\varphi \sim e^{-\beta_1 r}$). For sufficiently small ($E \lesssim 1$ eV) binding energies of the negative ions the "extra" electron moves far from the atom and hence the Schrödinger equation for the wave function of this electron contains the potential in (1):

$$\varphi'' + \beta_1^2\left(\frac{1}{x^4} - 1\right)\varphi = 0, \qquad (14)$$

where $\beta_1^2 = \sqrt{2\alpha\epsilon_i}$; $r = \sqrt{\alpha}\,x/\beta$; ϵ_i is the binding energy of the negative ion in atomic units.

To determine γ numerically it is convenient to make the substitution $x = 1/\xi$, $\varphi = \psi/\xi$; we thus obtain

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*tg = tan.

*ctg = cot.

$$\psi'' + \beta_1^2 (1 - 1/\xi^4)\psi = 0. \qquad (15)$$

The solution of this equation must satisfy the conditions

$$\psi|_{\xi\to\infty} = A \sin(\beta_1 \xi + \gamma), \qquad \psi|_{\xi\to 0} = B\xi \exp(-\beta_1/\xi).$$

The values of γ obtained in this way are approximated to an accuracy of 2% by the functions

$$\begin{aligned} \operatorname{tg}\gamma &= -\beta_1^2/(1 + 0{,}29\,\beta_1) && \text{for } 0 < \beta_1 < 1, \\ \gamma &= 0.47 - 1.12\,\beta_1 && \text{for } 1 < \beta_1 < 2. \end{aligned} \qquad (16)$$

When $\beta_1 \to 0$ we obtain the familiar formula $\tan \delta_0|_{k\to 0} = -\sqrt{E/\epsilon_i} = -\beta^2/\beta_1^2$. Equation (16) determines γ_s or γ_a depending on the multiplicity of the discrete level of the negative ion.

Thus, γ is expressed in terms of the binding energy of the negative ion; the cross sections for most atoms can be found this way.

C. In the case of the Ramsauer effect $\tan \gamma$ can be related to the value of the energy at which the cross section vanishes (neglecting p-scattering). The cross section $\sigma = 0$ when $\tan \delta_0 = 0$ i.e., when

$$A(\beta_{min}) = -\operatorname{tg}\gamma, \qquad (17)$$

where $\beta_{\min}$ is the value of β at which $\sigma = 0$. It is thus evident that the Ramsauer effect is possible when $\tan \gamma > 0$.

3. A knowledge of the energy dependence of the cross section can be used to find the mean frequency of collisions of electrons in the gas. For this purpose we compute the quantities $\overline{\sigma v}$, where the average is taken over a Maxwellian distribution:

$$\overline{\sigma v} = \frac{4\sqrt{T}}{\sqrt{2\pi m}} \int_0^\infty \sigma(Tx)\, x e^{-x}\, dx, \qquad (18)$$

and we have introduced the variable $x = E/T$. The mean value $\overline{\sigma v}$ is approximated to within 10% by the function

$$\overline{\sigma v} = \frac{4\sigma_0}{\sqrt{2\pi m\alpha}} \left[\frac{\sqrt{\alpha T}}{(1 + C(\gamma)\,\alpha T)^2} + \frac{D(\gamma)\,\alpha T}{(1 + C(\gamma)\,\alpha T)^{5/2}} \right]. \qquad (19)$$

The functions $C(\gamma)$ and $D(\gamma)$ are given below:

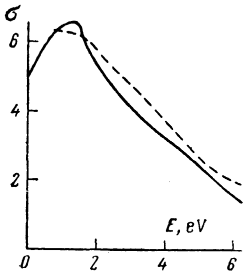
$\operatorname{tg}\gamma =$	—7	—5	—3	—2	—1,5	—1	—0.5	±0,1	0,5	1	1,5	2	2,5
$C =$	0,001	0.008	0,018	0.038	0.059	0,074	0.38	2,2	0.9	0.74	1.11	1.7	2,6
$D =$	5.45	3.65	1,96	1,13	0,69	0,36	0.15	0	0	0	0	0	0

The function in (19) is obtained by approximating $\sigma(E)$ for different values of γ and carrying out the integration. When $\tan \gamma > 0$ (the Ramsauer case), $\sigma(E)$ is approximated only up to $\sigma = 0$. Hence (19) applies for $T < E_{\min}$ where $E_{\min}$ is the energy at which $\sigma = 0$. It is not meaningful to use the approximation when $E > E_{\min}$ because $\sigma(E)$ rises sharply when $E_{\min} < E \lesssim 15$ eV. On the other hand, to carry out the integration in Eq. (18) with $T > E_{\min}$ we must know the behavior of $\sigma(E)$ up to $E \approx 10$ eV, where p-scattering becomes important. When $\tan \gamma < 0$ the approximation holds for $E < 54/\alpha$, i.e., $\alpha T < 20$.

4. We now consider several examples. The cross sections σ_0 have been determined for argon, krypton, and xenon for limitingly small energies starting with the values of $E_{\min}$[3] (the polarizability is taken from [5]). In the table we give values of σ_0 computed on the basis of the theory given here and values obtained from the shift of the higher levels of the atoms of alkali metals in these gases.[3]

In Fig. 1 we show the energy dependence of the scattering cross section in helium. The original data are $\sigma_0 = 5.75 \times 10^{-16}$ cm^2 [3] and $\alpha = 1.33$.[5]

Gas	σ_0, 10^{-16} cm^2	
	Present work	ref. [3]
Ar	9	7,1
Kr	36	34
Xe	110	116



Energy dependence of the scattering cross section (in units of πa^2); the solid curve is the theoretical curve and the dashed curve is the experimental curve.[3]

For atomic hydrogen, in which the binding energy of the negative ion $\epsilon_i = 0.75$ eV and $\alpha = 9/2$, using (16) we find the cross section for limitingly small energies $\sigma_0 = 110\pi a^2$. Since the spins of the electrons in the negative hydrogen ion are in opposite directions the cross section is that for singlet scattering.

As we have already indicated, the analysis in the alkali metals holds without considering p-scattering only if $E \sim 0.1$ eV. The methods used here can also be used to obtain expressions for the phases of the p-scattering; these will contain a constant which, in general, is unrelated to the constant γ. Thus, a determination of the total cross section requires four constants (in the alkali metals σ_s and σ_a must also be taken into account).

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