

# Low-energy resonance scattering of electrons by Thomas-Fermi atoms

N. B. Berezina and Yu. N. Demkov

Leningrad State University

(Submitted April 13, 1974)

Zh. Eksp. Teor. Fiz. 68, 848-854 (March 1975)

Scattering of electrons by atoms in the energy range from a fraction of an electron volt to the first excitation potential is considered within the framework of the statistical model. It is of interest to assess the exerted on the scattering process by the energy levels that emerge into the continuous spectrum as the charge on the atomic nucleus is decreased. The quasistationary states thus formed, whose width is calculated in this paper, may cause a number of broad resonances to appear in the slow-electron scattering cross section. Curves of the dependence of the resonance-scattering cross section on the incident-electron energy are presented for a number of atoms ( $22 \leq z \leq 26$ ) and from these it is possible to trace the variation of the shape and position of the resonances with variation of the nuclear charge  $z$ . The behavior of the scattering length near the points of contact of  $s$  levels with the edge of the continuous spectrum is analyzed.

The study of electron-atom elastic-scattering cross sections at low energies is interesting because of the presence in the cross-sections of numerous resonances, giving a wealth of information on the properties and structure of the atoms. In this paper we consider the theoretical possibility of the appearance of a special type of resonance, associated with the existence of quasi-stationary states of the negative ions of the corresponding atoms. These resonances should be observed in electron-atom scattering experiments.

Our approach is to trace how, as the nuclear charge  $z$  is varied, the bound states of an electron in the effective field of the atom emerge into the continuous spectrum, where they become quasi-stationary and produce the resonances under consideration. Our aim will be to study the general trends in the behavior of the cross sections, without taking into account the effect of the specific structure of each atom considered. This enables us to apply the statistical Thomas-Fermi model to describe the potential of the atom; this model has the added convenience, in our case, that in it the nuclear charge can be regarded as a continuously variable parameter. The latter circumstance makes it possible to apply the special modified perturbation theory proposed by Ostrovskii and Solov'ev<sup>[1]</sup> for states with a small binding energy. The application of the statistical potential to describe the scattering process is fully justified if the energy of the incident electron lies in the range from a fraction of an electron-volt to several electron-volts (below the atomic excitation potential). At lower energies long-range forces play an important role (these forces are also important at high energies in small-angle scattering).

In our previous paper<sup>[2]</sup> it was shown that for low energies the energy levels in the statistical potential are grouped in such a way that levels with the same value of the quantum number  $N = n + l$  emerge almost simultaneously into the continuous spectrum (the levels intersect the edge of the continuum simultaneously for the focusing potential  $-z/r(1+ar)^2$ , which is close to the statistical potential<sup>[3]</sup>). As is discussed in detail below, this leads also to a corresponding grouping of the low-energy resonances. In the paper, scattering cross sections are presented for some of the most interesting values of  $z$ , and the electron-atom scattering length is also calculated as a function of the nuclear

charge for the model potential. In the latter case we have succeeded in correcting important errors in the earlier calculations of Tietz<sup>[4]</sup>, who used the same model.

It follows from<sup>[2]</sup> that, despite the neglect of the Coulomb interaction experienced by an electron in a neutral atom at large  $r$ , reasonable results are obtained with regard to the sequential occupation of the energy levels. For the problem of scattering of an electron by a neutral atom the approximation of elastic scattering by the Thomas-Fermi potential is even more justified, since the Coulomb interaction at large distances is absent and the principal long-range term  $115/r^4$  in the potential corresponds to the actual polarization interaction  $\alpha/2r^4$  with a  $z$ -independent polarizability  $\alpha = 230$  (a quantity which can be regarded, in the standard sense, as the polarizability averaged over a period of the Mendeleev periodic table).

Of course, in a sufficiently exact calculation of the electron-atom scattering it is necessary to take into account the exchange interaction. This is especially important in order that the electron may not occupy those energy levels in the effective potential well that are already occupied by atomic electrons. Therefore, in these cases when the electron energy is comparable with the energy of atomic electrons, e.g., in the formation of a chemical bond, it is necessary to make such allowance for exchange. However, in the region of small positive energies, in which we are interested here, it may be assumed that representing the atom in the form of a local model potential is fully justified.

1. Let  $z_{nl}$  be those values of the nuclear charge  $z$  of the atom for which the state with the corresponding quantum numbers has the energy  $E_{nl} = 0$ . Then for  $z > z_{nl}$  the energy  $E_{nl} < 0$  and in the well there are bound states with principal quantum number  $n$  and orbital quantum number  $l$ . For  $z < z_{nl}$  the values  $n$  and  $l$  will correspond to quasi-stationary ( $l \neq 0$ ) or virtual ( $l = 0$ ) states, which give rise to resonance scattering at low energies. The values  $z_{nl}$  were calculated in the Thomas-Fermi approximation in<sup>[2]</sup>.

To describe scattering for  $z \lesssim z_{nl}$  we can make use of perturbation theory, assuming the difference  $V(r)$  between the potentials  $U(z_{nl}, r)$  and  $U(z, r)$  to be small. Perturbation theory for the case when the unperturbed

state lies on the boundary between the discrete and continuous spectra was considered in the paper by Ostrovskiy and Solov'ev<sup>[1]</sup>. Here we have applied the formulas they obtained to the determination of the position and width of the resonance energy levels as a function of  $z_{nl} - z$  in the Thomas-Fermi approximation.

We have considered the Thomas-Fermi potential of a neutral atom, satisfying the equation

$$\frac{1}{r} \frac{d^2(rU)}{dr^2} = -\frac{8\sqrt{2}}{3\pi} (-U)^{3/2} \quad (1)$$

with the boundary conditions

$$-rz^{-1}U(r) \xrightarrow{r \rightarrow 0} 1, \quad U(r) \xrightarrow{r \rightarrow \infty} 0. \quad (2)$$

A characteristic feature of such an atomic potential is the fact that all numbers  $z_{nl}$  with the same value of  $N = n + l$  are close to each other. They coincide exactly, as was shown in<sup>[3]</sup>, for the Tietz potential<sup>[6]</sup>:

$$U(z, r) = -z/r(1+ar)^2. \quad (3)$$

The additional degeneracy at  $E = 0$  is associated here with the presence of a special symmetry group.

In<sup>[1]</sup> a general formula was derived for the width  $\Gamma$  of the quasi-stationary states in a low-energy approximation. In our case the difference  $z_{nl} - z$  plays the role of the perturbation parameter. The perturbing potential in the Thomas-Fermi approximation is equal to

$$V(r) = 1/3 z_{nl}^{-1} [U'(z_{nl}, r) + 4U(z_{nl}, r)].$$

Then  $\Gamma_{nl}$  can be represented in the form

$$\Gamma_{nl} = \gamma_{nl} (z - z_{nl})^{l+1/2} + O(|z - z_{nl}|^{l+3/2}), \quad (4)$$

where

$$\gamma_{nl} = \lim_{R \rightarrow \infty} \frac{1}{2} \left[ \frac{2}{3z_{nl}} \int_0^R V(r) \varphi_{nl}^{(0)2} dr \right]^{l+1/2} \times \left[ \int_0^R \varphi_{nl}^{(0)2} dr \right]^{-l-3/2} \left[ \frac{\varphi_{nl}^{(0)}(R)R^l}{(2l-1)!!} \right]^2.$$

The functions  $\varphi_{nl}^{(0)}(r)$  satisfy the radial Schrödinger equation with zero energy:

$$\frac{d^2 \varphi_{nl}^{(0)}}{dr^2} - \frac{l(l+1)}{r^2} \varphi_{nl}^{(0)} - U(z_{nl}, r) \varphi_{nl}^{(0)} = 0, \quad (5)$$

and

$$\varphi_{nl}^{(0)}(r) \underset{r \rightarrow \infty}{\sim} r^{-l}, \quad \varphi_{nl}^{(0)} \underset{r \rightarrow 0}{\sim} r^{l+1}.$$

2. We can determine the position of the low-energy resonance if we know the derivatives of the energy with respect to the variable nuclear charge  $z$  at the points  $z_{nl}$ . It was shown in<sup>[3]</sup> that in the case  $l \neq 0$  a formula following from the Hellmann-Feynman theorem is valid:

$$E_{nl} = \left[ \int_0^\infty V(r) \varphi_{nl}^{(0)2} dr / \int_0^\infty \varphi_{nl}^{(0)2} dr \right] (z - z_{nl}); \quad (6)$$

for  $l = 0$  we have the special case<sup>[3]</sup>

$$E_{n0} = 2 \left[ \int_0^\infty V(r) \varphi_{n0}^{(0)2} dr / \lim_{R \rightarrow \infty} \varphi_{n0}^{(0)2}(R) \right] (z - z_{n0})^2 = 2(z - z_{n0})^2 \tau_{n0}. \quad (7)$$

Taking into account that we know the behavior of the wave-function in the field  $U = -\alpha/2r^4$ , i.e., in the long-range part of the Thomas-Fermi potential,

$$\varphi_{n0}^{(0)} \sim \text{const} \cdot r \sin((\alpha/2)^{1/4}/r)$$

we can determine the normalization constant in formula (7). For the case  $l \neq 0$  the normalization integral in formula (6) breaks down into two integrals

$$\int_0^R \varphi_{nl}^{(0)2} dr = \int_0^R \varphi_{nl}^{(0)2} dr + \int_R^\infty \varphi_{nl}^{(0)2} dr,$$

of which the first has been calculated numerically and the second analytically. In this we have used the asymptotic behavior of the function at infinity.

At sufficiently large distances  $r$  the Thomas-Fermi potential ceases to depend on the nuclear charge of the atom. Therefore, starting from a certain  $r = R$ , the difference  $V(r) = U(z_{nl}, r) - U(z, r)$  equals zero. This enables us to calculate the integrals in the numerators of formulas (6) and (7) with great accuracy.

3. In Table I we give the calculated values of the coefficients  $\gamma_{nl}$  in formula (4), corresponding to definite values of  $z_{nl}$  ( $l \neq 0$ ), and the values of  $\partial E_{nl}/\partial z$  at the points  $z_{nl}$ . A comparison of the values of  $z_{nl}$ , calculated for the Thomas-Fermi potential, with the actual appearance of the states  $nl$  in the periodic table shows that agreement is fairly good for  $s$ -states, and the size of the discrepancy does not exceed 1-3. This agreement worsens with increasing  $l$ ; nevertheless, for  $p$ -states and low  $z$  the calculated values of  $z_{nl}$  are quite reasonable.

It follows from (4) that

$$\Gamma_{nl} = \gamma_{nl} \left[ \frac{E_{nl}}{(\partial E_{nl}/\partial z)_{z_{nl}}} \right]^{l+1/2}. \quad (8)$$

Therefore, as  $n$  increases (for the same value of  $l$ ), which corresponds to a relative decrease of the height of the potential barrier, the ratio  $\gamma_{nl} (\partial E_{nl}/\partial z)^{l+1/2}$  should increase. This is confirmed by the numerical estimate given in the last column of Table I.

The values of the derivatives  $\partial E_{nl}/\partial z$  increase with increasing orbital quantum  $l$  for constant  $N = n + l$ , in agreement with the level-filling rule found earlier<sup>[3]</sup>. For comparison, the values of the derivatives  $(\partial E_{nl}/\partial z)_{\text{Tietz}}$  for the Tietz potential (3), where  $a$  was chosen to be  $0.643z^{1/3}$ , are also given in the table. Because of the incorrect asymptotic form of this potential at infinity ( $r^{-3}$ ) these values are always lower than the corresponding quantities calculated in the Thomas-Fermi potential. The difference is smaller, the greater is  $l$  and the smaller is  $z_{nl}$ .

Table II gives the values of the coefficients  $\tau_{n0}$  in (7) for the corresponding values of  $z_{n0}$ . They also decrease with increasing  $n$ .

4. From the data of Tables I and II we can construct an approximate picture of the behavior of the energy

TABLE I

$l$	$n$	$z_{nl}$	$\gamma_{nl}$	$(\frac{\partial E}{\partial z})_{nl}$	$(\frac{\partial E}{\partial z})_{\text{Tietz}}$	$\gamma_{nl} / (\frac{\partial E}{\partial z})_{nl}^{l+1/2}$
1	2	6.5	0.013	0.027	0.023	2.9
	3	14.5	0.0044	0.011	0.008	3.8
	4	27.5	0.0025	0.006	0.003	5.4
	5	47.5	0.0016	0.0042	0.0016	6.3
	6	74.0	0.0005	0.0017	0.0008	7.2
2	3	25.9	0.013	0.096	0.11	4.6
	4	43.8	0.0046	0.047	0.043	3.6
	5	68.7	0.0008	0.023	0.021	10.1
3	4	65.9	0.0034	0.18	0.21	12.9

TABLE II

$n$	$z_{n0}$	$\tau_{n0} \cdot 10^6$	$n$	$z_{n0}$	$\tau_{n0} \cdot 10^2$
2	2.8	6	4	17.5	0.37
3	8.2	2.6	5	33.5	0.27

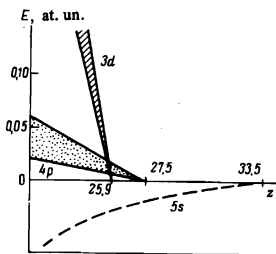


FIG. 1

FIG. 1. Behavior of the quasi-stationary (4p and 3d) and virtual (5s) energy levels. The energy is plotted in atomic units along the vertical axis, and the width of the "cones" corresponds to the width of the quasi-stationary states.

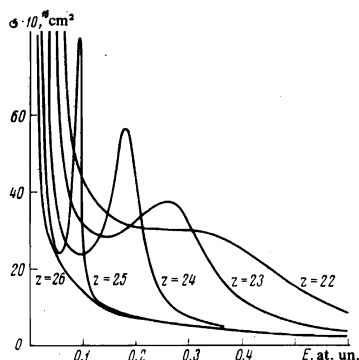


FIG. 2

FIG. 2. Cross section for elastic resonance scattering in the Thomas-Fermi approximation for atoms with different nuclear charges, as a function of the incident-electron energy.

levels near the boundary between the continuous spectrum and the quasi-stationary states of the atom, and, consequently, determine the cross-section for scattering of low-energy electrons. Especially interesting is the case when we consider atoms with nuclear charge close to a value  $z_{n,l}$ , and levels with the same number  $N$ .

Figure 1 shows the behavior of the 5s, 4p and 3d levels in the range of  $z$  from 25 to 34. The pattern of the dependence of the resonance-scattering cross-section on the incident-electron energy, which varies from 0.01 to 0.6 a.u., is shown in Figs. 2 and 3. The atoms from titanium ( $z = 22$ ) to iron ( $z = 26$ ) have been considered. In this range the 4p and 3d levels move out into the continuum. The cross-section is defined approximately as the sum of the partial cross-sections for  $l$  equal to 0, 1 and 2, which make the largest contribution to the scattering.

In all our calculations we have not taken into account the polarization potential, which plays a fundamental role at large distances from the nucleus. However, for  $l \geq 2$  a potential barrier already arises at the distances, not exceeding 2.5 a.u., which play the principal role in the calculations. Thus, with increasing  $l$  the calculations in the Thomas-Fermi potential become more and more justified.

5. One of the principal characteristics of elastic electron-atom scattering at low energies is the scattering length. Knowing its value, we can always determine the phase of the scattered wave and the scattering cross-section. A calculation of the scattering length in the Thomas-Fermi approximation has been performed by Robinson<sup>[7]</sup>. Of some interest, however, is the approximate analytic expression obtained by Tietz<sup>[4]</sup> for the scattering length  $a$  for the model potential

$$U(z, r) = -\frac{z}{r(1+cr)^2(1+dr)}, \quad (9)$$

where  $c = 0.57z^{1/3}$  and  $d = 0.049z^{1/3}$ . In this approximation,

$$a = -\left\{ z z^{F_1} \left[ \frac{3}{2} + \frac{1}{2} \left( 1 + \frac{8z}{c-d} \right)^{1/2}, \frac{3}{2} - \frac{1}{2} \left( 1 + \frac{8z}{c-d} \right)^{1/2}, 3; \frac{c-d}{c} \right] \right. \\ \left. \times \left\{ c^2 z^{F_1} \left[ \frac{1}{2} + \frac{1}{2} \left( 1 + \frac{8z}{c-d} \right)^{1/2}, \frac{1}{2} - \frac{1}{2} \left( 1 + \frac{8z}{c-d} \right)^{1/2}, 2; \frac{c-d}{c} \right] \right\}^{-1} \right\}.$$

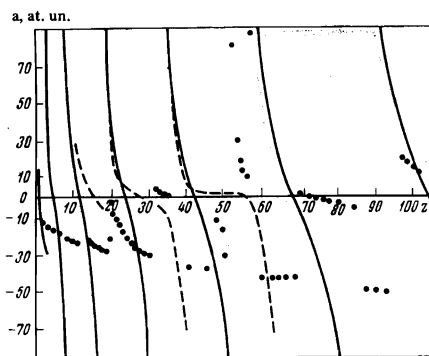


FIG. 3. Electron-atom scattering lengths in the Thomas-Fermi approximation (dashed curves), calculated by Tietz for the potential (9) (the dots), and calculated in this paper for the same potential (the solid curves).

Tietz noted the quasi-periodicity of the variation of  $a$  as a function of the nuclear charge  $z$ , playing the role of a parameter. However, the numerical data of his calculations appeared to us to be dubious. In particular, he cites<sup>[4]</sup> the following values of  $z_{n,l}$  at which the scattering length takes values of the order of  $10^{18}$  a.u.:  $z_{n,l} = 12, 19, 31, 38, 47, 58, 59, 85, 86, 94, 95$ . These values of  $z$  should correspond to the nuclear charges, at and above which the next bound state with  $l = 0$  appears in the atom. In the exact Thomas-Fermi potential<sup>[7]</sup>,  $z_{n,0} = 2.5, 7.5, 33.5, 17.5, 57.0, 57.0, 90.0$ , i.e., differs greatly from the values calculated by Tietz.

Figure 3 shows the findings for the scattering length, obtained in our work using the potential (9). The findings of Tietz are marked by dots. A comparison of the two calculations, and also the irregularity of Tietz's data, show that his calculations were erroneous.

Using the expression for the  $s$ -level energy in<sup>[8]</sup> and the effective-range approximation for the negative levels  $(2E_{n,0})^{1/2} = -1/a(z) + O(E_{n,0})$ , we obtain

$$\text{res}_{z=z_{n,0}} a(z) = -\lim_{r \rightarrow \infty} \int_0^{\infty} \Psi^2(z_{n,0}, r) / \int_0^{\infty} \Psi^2(z_{n,0}, r) U(z_{n,0}, r) dr.$$

Introducing the coefficients  $\tau_{n,0}$  by formula (7), for a we have

$$a(z) = -\tau_{n,0}^{-1/2} (z - z_{n,0}).$$

If we trace isoelectronic sequences of positive ions with  $N$  electrons, neutral atoms and negative ions, the energy required to detach an electron decreases monotonically with decreasing  $z$  and vanishes at a certain  $z = z_0$  close to  $N - 1$ . For lower  $z$  this state goes over into the continuous spectrum. If  $z_0 > N - 1$ , we may expect a low-energy resonance to appear in the cross-section for scattering of an electron by the neutral  $N$ -electron atom. An example is the alkaline-earth atoms, for which there are no negative ions and, therefore, low-energy  $p$ -resonances are possible.

Although the calculations based on the Thomas-Fermi approximation are rather crude, both with regard to the values of  $z_{n,l}$  themselves and with regard to the quantities characterizing the slope of the terms, they give, nevertheless, a sufficiently realistic indication of the grouping of the resonances in accordance with the  $n + l$  rule and of the intervals of  $z$  in which these resonances must be sought. The available experimental data do not, as yet, enable us to confirm or refute these predictions.

The authors are deeply grateful to Professor G. F. Drukarev, and also to V. N. Ostrovskii and V. V. Kuchin-

skii for their constant interest in the work and for useful discussions.

- <sup>1</sup>V. N. Ostrovskii and E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **62**, 167 (1972) [Sov. Phys.-JETP **35**, 89 (1972)].  
<sup>2</sup>Yu. N. Demkov and N. B. Berezina, Opt. Spektrosk. **34**, 841 (1973) [Opt. Spectrosc. (USSR) **34**, 485 (1973)].  
<sup>3</sup>Yu. N. Demkov and V. N. Ostrovskii, Zh. Eksp. Teor. Fiz. **62**, 125 (1972); **63**, 2336 (1972) [Sov. Phys.-JETP **35**, 66 (1972); **36**, 1233 (1973)].  
<sup>4</sup>T. Tietz, Z. Naturforsch, **26A**, 1054 (1971).

<sup>5</sup>N. F. Mott and H. S. W. Massey, Theory of Atomic Collisions, Oxford University Press, 1965 (Russ. Transl. "Mir", M., 1969).

<sup>6</sup>T. Tietz, Ann. der Phys. **12**, 373 (1964).

<sup>7</sup>L. B. Robinson, Phys. Rev. **117**, 1281 (1960).

<sup>8</sup>G. F. Drukarev, Teoriya stolknovenii elektronov s atomami (Theory of Electron-Atom Collisions), Fizmatgiz, M., 1963.

Translated by P. J. Shepherd.

94