A QUALITATIVE INTERPRETATION OF THE MEAN ELECTRON EXCITATION ENERGY IN ATOMIC COLLISIONS

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The transformation of the kinetic energy of the relative motion of colliding particles into the excitation energy of electrons is interpreted as resulting from their deceleration caused by an electron exchange. The motion of electrons in the region of overlapping shells of the colliding particles is considered quasi-classically. It is assumed that, when the electron moves out of the potential field of one of the atoms into that of another, it transfers from the first atom to the second a momentum which, on the average, is equal to the product of the relative velocity of the atoms and the mass of the electrons.

INTRODUCTION

THE majority of experiments on atomic collisions refer to a range of relative velocities of the atoms ($5 \times 10^6 - 10^8$ cm/sec) and of the impact parameters such that one of the excitation theories is not applicable in the first approximation. Thus, for example, it has been shown[1,2] that in collisions between the A atom and A^+ ion with energy equal to 75 kev (velocity equal to 6×10^7 cm/sec) and impact parameter $< 10^{-8}$ cm, the probability of secondary ionization is larger than the probability of elastic collision. However, even the first approximation of the theory of quasi-adiabatic perturbations which could be acceptable for the slowest velocities of the relative motion of atoms ($< 10^7$ cm/sec) turns out to be very complicated. It is very difficult to find the wave functions and the energy levels at all distances between the nuclei. The dependence of the terms on the distance between the nuclei is obviously very complicated, with a large amount of intersections in points where transitions from one term to another occur most frequently. Finally, the very approach of the atoms occurs for already excited states of the produced quasi-molecule, apart from a few exceptional cases. These are the cases where the orbital moments of both atoms equal zero and the sum of their spins is smaller than unity. (The energy level corresponding to separate atoms splits at their approaching each other into many levels, depending on the value of the projection of the atomic moments on the line joining the nuclei and the sum of their spins). The distances between excited levels are very small, and the adiabatic conditions are not fulfilled at comparatively low velocities.

The present paper represents an attempt to estimate at least the average energy of excitation of the electronic shells of colliding atoms using the ideas of classical mechanics. Unfortunately, this could not be sufficiently well based on theory but, from the experimental point of view, the procedure yields reasonable results. The calculation is applicable for distances between the neighboring energy levels of the system of colliding atoms which are small compared to the calculated mean energy of excitation of the electrons. This fact already negates with a high degree of probability, the application of the first approximation of any perturbation theory, since the distances of the first excited level from the ground state are of the same order of magnitude as the ionization energy.

The excitation energy of atomic shells is assumed to be distributed among all electrons and to be lost on ionization of the atoms at the end of the collision process or soon after it. Only that part of energy which is not sufficient for additional ionization can be emitted or be contained in a metastable state. This is connected with the fact, that the time of emission (of the order of $10^{-1} - 10^{-9}$ sec) is much longer than the time for the Auger effect ($10^{-15} - 10^{-14}$ sec) which, in turn, is somewhat longer than the time of collision.

If the average energy of excitation as a function of the relative velocity and of the impact parameter is known, then it is possible to estimate the effective cross section of various inelastic processes using, in addition, statistical considerations. Such an estimate has been carried out by Russel and Thomas.[3]

1. MUTUAL SLOWING DOWN OF ATOMIC NUCLEI DUE TO MOMENTUM TRANSFER BY ELECTRONS

For a sufficiently large number of electrons in each of the colliding atoms, the wave functions of the latter correspond to a high quantum state since they should be antisymmetric with respect to the permutation of electrons. This is also true as far as the wave function of the quasi-molecule constructed out of the atoms in the process of their collision is concerned. For large distances between the nuclei, $R = |\mathbf{R}_a - \mathbf{R}_b|$ the wave function is of the form

$$\Psi = \psi_a(\cdots \mathbf{r}_a \cdots) \exp\left(\frac{i}{\hbar} m\dot{\mathbf{R}}_a \Sigma \mathbf{r}_a\right) \psi_b(\cdots \mathbf{r}_b \cdots) \exp\left(\frac{i}{\hbar} m\dot{\mathbf{R}}_b \Sigma \mathbf{r}_b\right) \times \exp\left[-\frac{i}{\hbar}\left(E + N_a \frac{m\dot{\mathbf{R}}_a^2}{2} + N_b \frac{m\dot{\mathbf{R}}_b^2}{2}\right)\right], \quad (1)$$

where $\psi_a(\ldots \mathbf{r}_a \ldots)$ (N_a electrons) and $\psi_b(\ldots \mathbf{r}_b \ldots)$ (N_b electrons) are the wave functions of atoms for stationary nuclei, $\mathbf{r}_{a,b}$ are the coordinates of electrons and $\dot{\mathbf{R}}_{a,b}$ are the velocities of the atomic nuclei. Evidently, it is necessary to carry out a permutation of electrons belonging to various atoms.

The exponential factors indicate the fact that the average velocity of each electron is identical with the velocity of the atom to which it belongs, and that the kinetic energy due to the motion of the atom as a whole must be added to the energy of electrons in stationary nuclei. The relation between the mean electron velocity and their position with respect to the nuclei is in some manner conserved in the collision process. In that main part of the distribution of the electron concentration in atoms or molecules, the energy of the interaction of electron pairs is equal to $\sim e^2 n^{1/3}$, (where e is the charge and n the concentration of electrons) and is small with their kinetic energy $\sim \hbar^2 n^{2/3}/2m$. The motion of electrons takes place to a first approximation, in the field of electrons and nuclei determined from the Thomas-Fermi model.

The Thomas-Fermi potential has on the line connecting the atomic nuclei a saddle-type minimum, through which we shall construct a surface S perpendicular to the equipotential surfaces. (For different charges of the atomic nuclei, this is an infinite surface perpendicular to the line connecting the nuclei, and dividing it into two). From the Gauss theorem we know that if the quasi-molecule is neutral on the whole, then the total charge of electrons which on the average are present on one side of this surface is equal to the charge of the corresponding nucleus.

For a motion in the direction of the corresponding nucleus along this surface, or any equipotential surface, the potential increases faster than the inverse distance to this nucleus. Trajectories of electrons moving in such fields according to the laws of classical mechanics would in general be loops or even twisting and untwisting spirals.

It is therefore natural to assume that the surface S divides the regions of the action of the potentials of the first and second atom. Passing through S, the electrons strongly interact with the field of the corresponding atom, losing their initial momentum and, on the average, assuming a momentum corresponding to the velocity of the atom. The electron flux density through the element of area dS in one direction is nv/4, where v is the mean value of the absolute velocity. (We assume that the velocity distribution of electrons is spherically symmetric). The total momentum transfer, i.e., the force acting on the corresponding atom, will be given by the formula

$$\mathbf{F} = \pm m(\dot{\mathbf{R}}_a - \dot{\mathbf{R}}_b) \int_S \frac{nv}{4} dS. \quad (2)$$

A similar force with opposite sign acts on the atom. The work done by these forces moving the atoms for a distance $d\mathbf{R}_a$ and $d\mathbf{R}_b$ is equal to $\sim -m(\dot{\mathbf{R}}_a - \dot{\mathbf{R}}_b)\, d(\mathbf{R}_a - \mathbf{R}_b)$ or, denoting $d\mathbf{R}_a - d\mathbf{R}_b = d\mathbf{R}$, we obtain for the total work of slowing down the atoms (in other words, the electron excitation energy)

$$\mathcal{E} = m \int \left(\int_S \frac{nv}{4} dS\right) \dot{\mathbf{R}} d\mathbf{R}. \quad (3)$$

Assuming that the interaction does not very strongly affect the expression given by the Thomas-Fermi model, $v = \frac{3}{4}(3\pi^2)^{1/2}\hbar n^{1/3}/m$,

$$\mathcal{E} = \frac{3}{16}(3\pi^2)^{1/3}\hbar \int \left(\int_S n^{4/3} dS\right) \dot{\mathbf{R}} d\mathbf{R}, \quad (4)$$

or, expressing n in terms of the potential φ using $n = 2^{3/2}(me\varphi)^{3/2}/3\pi^2\hbar^3$, and substituting into Eq. (4), we have

$$\mathcal{E} = \frac{m^2 e^2}{4\pi^2\hbar^3} \int \left(\int_S \varphi^2 dS\right) \dot{\mathbf{R}} d\mathbf{R}. \quad (5)$$

In deriving Eq. (2), we did not take into account the transfer of momentum due to the exchange of electrons (or to the collision of electrons belonging to various atoms) since the corresponding force of repulsion between the atoms is also present for stationary atoms and is a part of the conservative forces.

In addition, it was assumed $|\dot{\mathbf{R}}| \ll v$. In the opposite case, the momentum transport would be much smaller.

2. ESTIMATE OF THE MEAN EXCITATION ENERGY OF ELECTRONS ACCORDING TO EQ. (5)

Taking into account the qualitative character of Eq. (5), several other simplifications have been made in the following calculation.

1. If the discussion is limited to small-angle scattering, the motion of the nuclei is assumed to be rectilinear and uniform (the loss of kinetic energy is small compared to its initial value). We have then $\dot{\mathbf{R}}d\mathbf{R} = udx$, where $u = |\dot{\mathbf{R}}|$, $dx = \dot{\mathbf{R}}d\mathbf{R}/|\dot{\mathbf{R}}|$, and

$$\int\left(\int_S \varphi^2 dS\right)\mathbf{R}d\mathbf{R} = u\int_{-\infty}^{\infty}\left(\int_S \varphi^2 dS\right)dx. \tag{6}$$

From Eqs. (5) and (6), we obtain, taking φ and all linear dimensions in atomic units (for a potential e/a_0, $a_0 = \hbar^2/me^2$),

$$\mathscr{E} = \frac{\hbar u}{4\pi^2 a_0}\int_{-\infty}^{\infty}\left(\int_S \varphi^2 dS\right)dx. \tag{7}$$

2. If the nuclear charges of the atoms differ by not more than approximately four times, then, with a good accuracy, we can assume the surface S to be a plane perpendicular to the line connecting the nuclei and dividing it in two. For the potential φ at this plane, we assume

$$\varphi = \frac{Z_a + Z_b}{r}\chi(1.13\,[Z_a + Z_b]^{1/3} r), \tag{8}$$

where r is the distance from the point of the plane to one of the nuclei. Furthermore, since $dS = 2\pi\rho\,d\rho$, and $r^2 = (R/2)^2 + \rho^2$, we introduce a new variable ξ

$$\xi = 1.13\,(Z_a + Z_b)^{1/3}\sqrt{(x/2)^2 + \rho^2},$$
$$\xi_0 = 1.13\,(Z_a + Z_b)^{1/3} R_0/2, \tag{9}$$

where R_0 is the minimum distance between the nuclei ($R^2 = R_0^2 + x^2$), and transform Eq. (7) with potential φ determined by Eq. (8) into

$$\mathscr{E} = \frac{1.77}{\pi}(Z_a + Z_b)^{1/3}\frac{\hbar u}{a_0}\int_0^{\infty}\chi^2\left(\sqrt{\xi_0^2 + \xi^2}\right)\frac{\xi^2 d\xi}{\xi_0^2 + \xi^2}. \tag{10}$$

The integral in Eq. (10) is evaluated numerically and can be well approximated by the function

$$f = 0.61/(1 + 0.285\,\xi_0)^5 \tag{11}$$

up to the value of $\xi_0 = 6$. For large values of ξ_0, Eq. (11) gives a slightly lower value than the integral in Eq. (10).

We have, therefore

$$\mathscr{E} = \frac{0.35\,(Z_a + Z_b)^{5/3}\,\hbar u/a_0}{[1 + 0.16\,(Z_a + Z_b)^{1/3} R_0/a_0]^5} \tag{12}$$

or, in electron-volts

$$\mathscr{E} = \frac{(Z_a + Z_b)^{5/3}\,4.3\cdot 10^{-8} u}{[1 + 3.1\,(Z_a + Z_b)^{1/3} 10^7 R_0]^5} \tag{13}$$

where u is expressed in cm/sec and R_0 in centimeters.

3. COMPARISON WITH EXPERIMENT

Direct measurements of the average energy loss are known only for collisions of the ions of A^+ and Ne^+ at an energy of 75 kev with the atoms of A (experiments of Abrosimov and Fedorenko[2] on the scattering of argon target atoms at angles in the range of 84 to 78°). Theoretical values of the impact parameter R_0 necessary for calculations are taken from reference 4. We obtain the following table for the values of $\mathscr{E}$:

TABLE I

	75 kev $A^+ + A$, $u = 6\times10^7$ cm/sec				75 kev $Ne^+ + A$, $u = 8.5\times10^7$ cm/sec			
ϑ, deg	84	82	80	78	84	82	80	78
$10^9\cdot R_0$	2.3	1.9	1.7	1.54	2.2	1.8	1.54	1.48
$\mathscr{E}_{theor}$, ev	340	400	440	510	350	410	450	510
$\mathscr{E}_{exp}$, ev	380	640	890	990	490	560	750	940

The largest value of the mean average energy loss, as far as it can be judged from an extrapolation of the experimental data, is ~ 1500 ev for collision of $A^+ + A$ and $Ne^+ + A$, while the theoretical value for both cases is ~ 1000 ev.

Apart of this direct comparison with the experiment (other data for direct comparison are not yet available), we can make an indirect comparison.

By solving Eq. (13) with respect to R_0, we can obtain the cross section πR_0^2 for an average electron excitation energy exceeding $\mathscr{E}_0$. Inelastic processes that require an energy greater than $\mathscr{E}_0$ will have in this case a lesser probability. On the other hand, if the excitation energy is greater than the ionization energy, ionization occurs with a high probability since the time of emission is large compared with the time of the Auger effect which is comparable with the collision time.

Assuming, therefore, that $\mathscr{E}_0$ is equal to the smaller ionization energy of the two colliding atoms, one can approximately estimate the cross section for removing electrons as a function of the relative velocity of atoms and the number of electrons in then:

$$\pi R_0^2 = 3.3\cdot 10^{-15}(Z_a + Z_b)^{-2/3} \times [((Z_a + Z_b)^{1/3} 4.3\cdot 10^{-8} u/\mathscr{E}_0)^{1/3} - 1]^2 \text{ cm}^2 \qquad (14)$$

($\mathscr{E}_0$ in ev). Introducing the characteristic velocity and cross section for each pair of colliding atoms

$$u_0 = [23\cdot 10^6 \mathscr{E}_0/(Z_a + Z_b)^{1/3}] \text{ cm/sec},$$

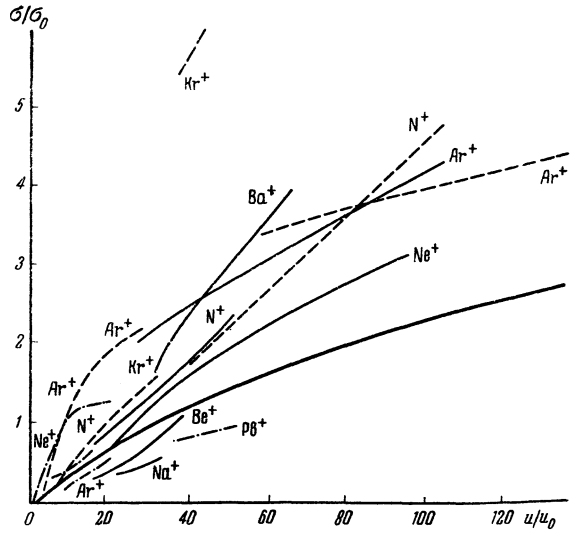
$$\sigma_0 = [33\cdot 10^{-16}/(Z_a + Z_b)^{2/3}] \text{cm}^2, \qquad (15)$$

the formula (14) can be written in the form

$$\sigma/\sigma_0 = [(u/u_0)^{1/3} - 1]^2, \qquad (16)$$

which gives a universal dependence for the cross section for the removal of electrons for any colliding pair as a function of their relative velocity.

Such a comparison with the available experimental data was carried out by N. V. Fedorenko. This comparison is given in the figure and in Table II, with his kind permission.



Dependence of the cross section of electron removal in colliding pair of atoms on the relative velocity in A (solid curve), Kr (dotted curve), and Ne (dot-dash curve). Solid, heavy line—theoretical.

4. DISCUSSION OF RESULTS

Comparison with the experiment, both direct and indirect, shows that experimental and theoretical data differ essentially by not more than a factor of two (with a few exceptions in the indirect comparison). It should be noted that, in the indirect comparison with the experiment, we studied eight different pairs of colliding atoms which are greatly different both in the total charge (from $N^+ + Ne$, $Z_a+Z_b = 16$ to $Pb^+ + Ne$, $Z_a + Z_b = 92$; $Ba^+ + A$, $Z_a + Z_b = 73$), and with respect to the ratio of their charge. The range of the relative velocities varies by a factor of ~ 30. From a comparison of $Ba^+ + A$ and $Pb^+ + Ne$, it can also be seen that the deviation of experimental data from theory is not due to an incorrect dependence on the sum of charge or on their ratio (the deviations are in both directions), but rather to individual peculiarities. The latter cannot be taken into account in the theory if the motion of electrons is considered according to the statistical model of Thomas and Fermi.

As to the direct comparison with the experiment, the theoretical result shows a weaker dependence of the mean energy of excitation on the impact parameter than that obtained experimentally. Obviously, this deviation is within the limits of accuracy of the calculation since, first, there is no solution for the Thomas-Fermi equation for two nuclei and, second, the impact parameter may be uncertain by as much as 10 or 20%. The theory given above cannot be expected to show a better agreement with the experiment, especially if one takes into account the roughness of the calculation carried out within its framework and the indirect character of the comparison with the experiment. We would still like to mention that the deviation of some experimental points in the direction of increasing cross section

TABLE II

Pair	$\sigma_0\cdot 10^{16}$, cm²	$u_0\cdot 10^{-8}$, cm/sec	Velocity range 10^6 cm/sec	Reference	Pair	$\sigma_0\cdot 10^{-16}$ cm²	$u_0\cdot 10^{-8}$, cm/sec	Velocity range 10^6 cm/sec	Reference
$N^+ + Ne$	4.94	4.48	25÷65	[5]	$Ar^+ + Ar$	—	—	24÷95	[6]
$Ne^+ + Ne$	4.44	3.42	3.42÷14.0	[7]	$Ba^+ + Ar$	1.86	0.281	8.5÷18	[5]
$Ne^+ + Ne$	—	—	22.5÷63.0	[7]	$Be^+ + Ar$	4.17	2.11	32÷80	[5]
$Ar^+ + Ne$	3.54	1.95	16.5÷39.0	[5]	$N^+ + Kr$	2.70	0.642	25÷66	[5]
$Pb^+ + Ne$	1.61	0.269	9.5÷13.7	[5]	$Ar^+ + Kr$	2.29	0.423	1.1÷11.4	[7]
$N^+ + Ar$	3.82	1.68	26÷65	[5]	$Ar^+ + Kr$	—	—	24÷60	[6]
$Na^+ + Ar$	3.46	1.33	28÷43	[5]	$Kr^+ + Kr$	1.89	0.262	1.8÷8.0	[7]
$Ne^+ + Ar$	3.54	1.41	30÷132	[6]	$Kr^+ + Kr$	—	—	10÷12	[7]
$Ar^+ + Ar$	3.00	0.91	2.2÷10	[7]					

can be explained. First, when the velocity of relative motion is much greater than the minimal necessary for the ionization, the cross section for double or even triple ionization has the same order of magnitude as for single ionization. Therefore, two or three electrons respectively are often captured in the collision, thus increasing the cross section. Secondly, as mentioned in the beginning of this article, in collisions, the quasi-molecule is produced adiabatically already in the excited state, and if the removal of an electron occurs at a comparatively small distance between the atoms, then the energy of removal may be two to three times smaller than the energy of ionization for far away atoms.

Correspondingly, the ratio u/u_0 will be three times larger. Taking into account these two facts, the discrepancy with experiment will be much smaller.

In any case, formula (16) gives the cross section for ionization for any pair of colliding atoms and in greater range of relative velocities with an accuracy to a factor of two.

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