One- and two-electron detachment from I^- in single rare-gas collisions

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Cross sections for the production of fast I^0 and I^+ particles from I^- negative ions in single collisions with He, Ne, Ar, Kr, and Xe targets are reported. The single-electron-detachment cross sections, which previously have been found to reach roughly constant values in other targets at about 100-eV center-of-mass energy, continue to rise until about 8 keV in neon, supporting the suggestion that the (I^-Ne) molecular state does not cross into the continuum. The double-electron-detachment cross sections do not show the inverse target-mass dependence which has been found for F^-—rare-gas double-electron-detachment collisions.

I. INTRODUCTION

Electron detachment from negative ions has been extensively investigated in the last few years, and the main features of the process in which a single valence electron is detached are beginning to be understood (for a review, see Risley[1]). It has been found that, in the energy region where the molecular-orbital approximation is valid, the detachment of the valence electron takes place either by direct excitation into an unbound state, or indirectly through the decay of an autodetaching metastable negative-ion state which is formed from either the target atom or the beam negative ion. Among the theories to describe the direct electron-detachment process, the local complex potential model has been quantitatively successful in fitting low-energy cross sections (Lam *et al.*[2]), but predicts decreasing cross sections at higher energies in conflict with the experimental measurements. The zero-range model (Demkov,[3] Guayacq[4]) includes tunneling from the bound state to the free-electron state, a process which increases with the collision energy, and in principle this model is able to fit the measured cross sections at higher energies, even though it has only been formulated for *s*-shell electron detachment. The I^--Ne electron-detachment cross section has been found to be anomalous in the low-energy region in that (a) it has a lower threshold energy of 3.0 eV compared to 7.8—8.0 eV for other I^-—rare-gas electron-detachment thresholds (Haywood *et al.*[5]), (b) the cross section up to 2 keV is about a tenth of the cross section which is expected if it fitted the systematic behavior of the other rare-gas targets (Bydin and Dukel'skii[6]), and (c) the peak in the electron spectrum at 6—7 eV which is observed in the other I^-—rare-gas collisions[7] is absent for the neon target.[8] This anomalous behavior is attributed by De Vreugd *et al.*[9] to the absence of a crossing between the initial state and the continuum of free-electron states, so that the I^-Ne system provides an experimental situation where only the zero-range model is appropriate to describe the detachment. Gauyacq[10] has successfully fitted the similar noncrossing case of the $(HNe)^-$ system with the zero-range theory.

The double-electron-detachment process in which two electrons are removed from the negative ion during a single atomic collision was first identified by Dukel'skii and Fedorenko[11] for several negative ions, including iodine, in nitrogen and argon gases. They noticed that the cross sections were large enough to contribute significantly to the total electron-detachment cross sections above about 5 keV when these are measured by electron collection techniques. Much less is known about this double-electron-detachment process than single-electron detachment. A few measurements are available for halogen negative ions,[12] which have closed-shell electronic structures, and these support the initial conclusion of Dukel'skii and Fedorenko that the cross sections contribute significantly to the total electron-detachment cross section. It can be concluded that there is a large probability that a second electron will be detached in all those collisions which detach one electron. On the other hand, recent measurements[13] with Li^- ions which have two electrons outside a closed shell indicate, rather surprisingly, that for these negative ions the double-electron detachment is much less likely, with cross sections only a few percent of the single-electron-detachment cross section.

Previous I^- double-electron-detachment cross-section measurements include the original identification of the double-electron-detachment process in which Dukel'skii and Fedorenko[11] measured the cross section for an argon target up to 17.5 keV, measurements of single detachment on all the rare gases except neon by Bydin and Dukel'skii[6] up to 2 keV, measurements of single-electron detachment on neon up to 3.6 keV by Hasted,[14] and measurements of both the total electron-detachment cross section and the double-electron-detachment cross section above 20 keV by Lichtenberg *et al.*[15]

II. EXPERIMENTAL METHOD

The apparatus consisted of a gas target 3.81 cm long with a 0.8-mm-diam entrance and a 1.5-mm-diam exit slit. The pressure in the target was controlled by a thermal-mechanical leak and measured with a capacitance manometer through separate offset pipes. Measurements were made throughout the range of pressures from the residual gas pressure up to 8×10^{-4} Torr. The background pressure on either side of the differentially pumped target was about 5×10^{-7} Torr. A third collimating slit 0.8 mm in diameter and 20 cm away from the entrance slit defined the direction of the incident negative ions to within $\pm0.2°$. The iodine negative ions were produced in a conventional RF-type ion source, running on argon but with a crystal of iodine in the gas supply pipe to this source on the low-pressure side of the thermal-mechanical leak. The iodine partial pressure was controlled by varying the temperature of the pipe by placing it in cooled water. Positive ions were extracted from the RF plasma and converted to negative ions by electron-capture collisions with the gas during their passage through the canal. After acceleration, a 90° deflection, 66-cm-radius magnet selected the I$^-$ beam from other negative ions.

Beyond the target a 5 cm length of transverse electric field separated the charge states of the ions from the target, and three channel electron multipliers, all with 1-cm-diameter cones, were set side by side to measure simultaneously the counting rates of the negative, neutral, and positive fast particles from the target. The geometry was such that all particles which had been scattered by angles up to $\pm2°$ during their passage through the target would strike the cone of the appropriate channel multiplier. It is difficult to determine the absolute detection efficiency of a Channeltron because pulse counting is only quantitatively accurate for beam intensities which are too small to measure by Faraday-cup techniques. Müller *et al.*[16] calibrated the efficiency of a Channeltron counting system by placing it behind a small hole in the end of a Faraday cup and averaging out beam nonuniformities by mechanical movements. They obtained 95% efficiency, in good agreement with a method which compares the same atomic cross section measured at low intensity using Channeltrons and at higher intensity using Faraday cups. It is known that the gain of a coned Channeltron varies with the location at which the heavy particle strikes.[17] In particular a particle which travels directly down the central hole rather than striking the cone has less length of secondary emission surface to multiply the electron current and so may produce smaller pulses. However by operating with sufficient voltage so as to be well into the pulse saturation regime, and counting all pulses with amplitudes above the dark current, these coned Channeltrons can be made to have the same counting efficiency for energetic ions everywhere over the acceptance aperture out to near the edge of the cone. This suggests (a) that this constant efficiency is near to 100%, and (b) the efficiency should be nearly the same for positive, neutral, and negative ions. The negative-ion counting rate was limited to 1 kHz to avoid pileup effects. This gave neutral- and positive-ion rates which were well above the dark current background except at the lowest target gas pressures.

The $\pm2°$ acceptance angle for the detection of the detached particles excludes some large-momentum-transfer collisions. No data on angular distributions are available at our energies, but measurements by Fayeton *et al.*[18] at 1 keV for Cl$^-$ on Ne indicate that the reduced differential cross section $\theta\sigma(\theta)\sin(\theta)$ peaks at about 2° and then falls off rapidly. The product of beam energy and scattering angle $(E\theta)$ is approximately an invariant of many scattering processes[19] so that there is unlikely to be significant contribution to the σ_{-0} cross section beyond 2° at our much higher beam energies. The σ_{-+} cross section has a larger energy defect and so should produce larger momentum transfers. Fayeton *et al.* found that $\theta\sigma_{-+}(\theta)\sin(\theta)$ reached a maximum at their largest scattering angle 6°. However, the reduced differential cross section overemphasizes the importance of larger angles, and $2\pi\sin(\theta)\sigma_{-+}(\theta)$, whose integral over θ is the total cross section, peaks at about 5 keV deg. It seems possible that several percent of the σ_{-+} cross section is missed by the 20-keV-deg limit in our 10 keV measurements, with smaller losses at higher energies.

III. DATA ANALYSIS

Both the single- and the double-electron-detachment cross sections were calculated from measurements of the ratio N of the neutral- or the positive-ion counting rate to the negative-ion counting rate, determined at a number of target gas pressures. A general relation for the cross section for the change of charge from an initial value i to a final value j is given by

$$T\sigma_{ij}=\frac{N}{1+N/2}\times\left\{1+\frac{1}{2}\left[\sigma_{ji}+\sum_k\left[\sigma_{jk}-\sigma_{ik}-\frac{\sigma_{ik}\sigma_{kj}}{\sigma_{ij}}\right]\right]T\right\},$$

where $i=-1$ for the negative-ion beam and j is either 0 or $+1$ for the single-electron- and double-electron-detachment cross sections, respectively. The summation excludes both $k=j$ and $k=i$. This equation is valid to first order in the target thickness $T=nL$, where n is the atomic density and L is the length of the gas target and is derived in the Appendix. A linear least-squares fit to the right side of the equation as a function of target gas pressure was made. The slope, after changing the target pressure to atomic density units gives the absolute cross section. The error from the least-squares fit was used to estimate the statistical error on the cross section. A small correction for the nonzero intercept of the linear relation was due to electron detachment by residual gas in the 2.5 m length of vacuum between the magnet and the target. A correction was made assuming that the residual gas had the same cross sections as the target gas.

If multiply ionized states are neglected then the summations over k reduce to a single term. For the σ_{-0} cross section, $k=+1$, and for σ_{0+} $k=0$ only. The σ_{-0} and σ_{-+} cross sections were first calculated without the target-thickness correction and then these first-order results were inserted into the correction term to obtain the final values. The next largest cross sections in the target-thickness corrections after the σ_{-0} cross sections were σ_{0+} and σ_{+0} which have both been measured by Layton and Fite,[20] but only for argon between 30 and 70 keV. These values were extrapolated to higher and lower energies using a typical energy dependence for these electron-transfer collisions. The same cross-section values were assumed for Kr and Xe. Calculations using a generalized noncrossing theory of electron transfer[21] indicated that for the helium target these cross sections are negligible in the correction term. On the other hand this theory predicted larger σ_{+0} cross sections for heavier targets, reaching 10^{-15} cm^2 for xenon. No measurements of σ_{0-} have been reported, but this process is expected to be small at our energies and was set to zero. The double-electron-transfer process σ_{+-} was also neglected.

The reproducibility of results was found to be somewhat worse than the statistical error on the slope of the least-squares fit, perhaps from short-term fluctuations in the beam, though the cross section was found not to be dependent to any measurable extent on the beam intensity. To obtain an estimate of the reproducibility, data previously published[22] on the F^- σ_{-0} cross section for a Ne target was reanalyzed. This had been obtained with the same apparatus and, because it shows no sign of energy variation over the entire energy range of the measurements, the individual variations about the mean of all the cross sections provide a measure of the reproducibility. The standard deviation was found to be 4.5%. A similar fit to the Cl^- σ_{-0} cross section for Ne gave a 6% reproducibility assuming a very slight linear decrease in the cross section with energy. In the σ_{-0} cross section there are large numbers of counts, but in the σ_{-+} cross section the positive-ion counts are less, typically a few hundred, so that there is an additional statistical error which was added to the error estimate for each σ_{-+} cross section.

Because the cross sections in the target-thickness correction are not well known, the target gas pressures were kept below 8×10^{-4} Torr so that the correction terms changed the calculated results by less than 1% for the σ_{-0} cross section. However, changes up to 9% in the σ_{-+} cross section occurred due to the presence of the large σ_{0-} values in the correction terms. As a check the highest pressure reading in each measurement was omitted in the calculations and it was then found that this changed the results mostly by much less than 1% and randomly in sign. The exception was with the xenon target where the large σ_{0-} and σ_{+0} values gave changes up to 3%. The error estimates for these results were increased to include this uncertainty. The absolute calibration of the capacitance manometer, which had been in use for several years, was checked by connecting a second identical new manometer through a separate pipe into the target. A comparison of the two readings during measurements gave a 3% difference in the absolute calibrations. The geometrical length of the target was accurately known, and the end corrections, assumed to be of the same order as the slit diameters, were also small enough to neglect.

IV. RESULTS AND DISCUSSION

A. Single-electron detachment

The results are shown in Table I and compared with previous measurements in Fig. 1. The Lichtenberg *et al.*[15] data was obtained by subtracting their values of σ_{-+} from σ_{tot} which they obtained by beam attenuation measurements. With the subtractions their values for the argon target are in good agreement. The lower-energy data of Bydin and Dukel'skii[6] extrapolates well to our lower-energy data except for krypton where there values are higher than our lowest-energy data.

The general trend of the single-electron-detachment cross sections seems to be a rise to an approximately con-

TABLE I. Cross section σ_{-0} for charge neutralization of I^- ions in collisions with rare-gas targets (10^{-16} cm^2). The total error is estimated to be about 6%.

Energy (keV)	Target $_2$He	$_{10}$Ne	$_{18}$Ar	$_{36}$Kr	$_{54}$Xe
10	5.2	2.8	7.5	7.6	8.5
20	4.8	7.2	8.9	8.9	8.2
30	5.0	6.1	8.8	8.9	9.5
40	5.2	5.9	8.6	9.3	9.5
50	5.3	5.6	8.3	9.5	10.0
60	5.5	5.6	8.9	9.8	9.8
70	6.3	5.8	8.9	11.0	10.0
80	6.2	5.6	9.1	10.0	10.0
90	6.2	5.4	9.6	11.0	10.0
100	6.2	5.5	9.7	11.0	9.7

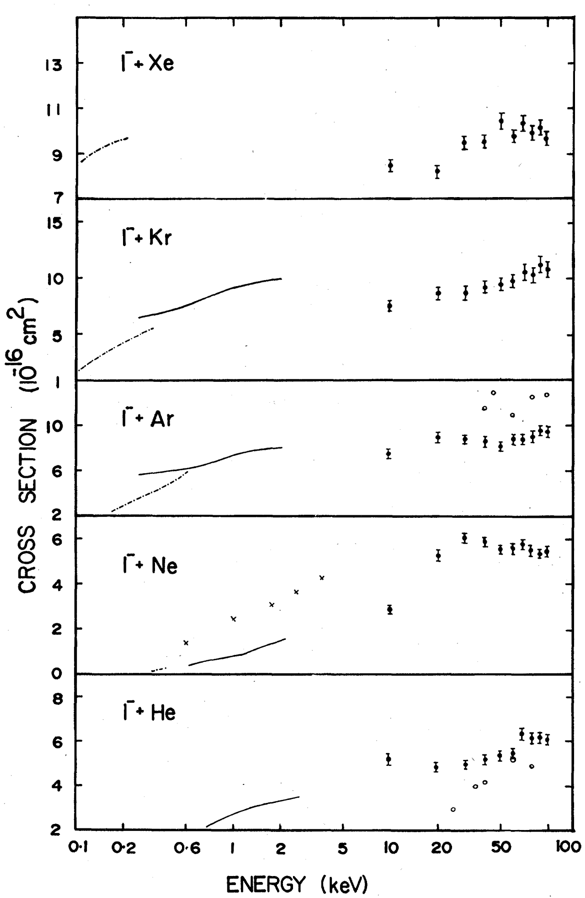

FIG. 1. The single-electron-detachment cross section σ_{-0}. Open circles are the data of Lichtenberg *et al.*[15] The continuous lines are the data of Haywood *et al.*[5] The crosses are the data of Hasted.[14] The present data are shown with error bars.

stant value at an ion energy which is reached at about 200 eV in xenon, but not till several keV in helium. These correspond to a center-of-mass collision energy of about 100 eV for both targets. Champion and Doverspike[23] were able to obtain excellent quantitative fits to low-energy single-electron-detachment cross sections from Cl^- ions on several rare-gas targets using the local complex potential model with interaction parameters derived from differential scattering data. These cross sections all showed this rise to a maximum at a center-of-mass collision energy of about 100 eV. It seems likely that the low-energy data for electron detachment from I^- in collisions with He, Ar, Kr, and Xe could be fitted with the complex potential model, assuming a crossing to the continuum, if scattering data were available. The absence of a crossing of the state $(INe)^-$ with $(INe+e)$, which has been suggested by Haywood *et al.*,[5] probably accounts for the anomalously low σ_{-0} cross section at low energies and then the gradual rise to about 4 keV center-of-mass collision energy, when a constant value is reached in the dynamic interaction region.

B. Double-electron detachment

The measurements shown in Table II confirm the relatively large magnitude of the double-electron-detachment cross section. In helium it is about 10% of the total cross section rising to more than 50% in xenon at our highest energies. The values are in good agreement with the previous argon data of Lichtenberg *et al.* and the original measurements of Dukel'skii and Fedorenko, though our helium data are somewhat larger.

In previous measurements of the double-electron detachment from F^- in rare-gas collisions, two unusual features were observed. The cross section was experimentally identical to the σ_{0+} cross section in the same target at the same energy, and the smallest cross sections occurred for the heavier targets Xe, Kr, and Ar, and the lighter atoms Ne and He had larger double-electron-detachment cross sections. These can be explained by the sequential nature of the double-electron-detachment process, so that the neutral molecular state (F + rare-gas atom) which is formed after direct detachment of the first electron is the same as the initial state in neutral fluorine—rare-gas collisions. The positive ions are then formed by crossings, at smaller interaction radii with states which are unstable to ionization. If the target has a lower ionization potential than fluorine, then molecular states which correspond to an ionized target will be crossed before states which result in F^+ production and therefore the σ_{-+} cross section for F^- production is re-

TABLE II. Cross section for the production of I^+ ions from I^- in single collisions with rare-gas targets (10^{-16} cm^2). The total error is estimated to be 10%, except for Xe where the error is about 13%.

Energy (keV)	$_2$He	$_{10}$Ne	Target $_{18}$Ar	$_{36}$Kr	$_{54}$Xe
10	0.09	0.03	0.50	0.46	0.64
15	0.30	0.03			
20	0.46	0.14	1.9	1.8	1.2
30	0.83	0.25	3.1	1.8	1.1
40	0.95	0.31	3.3	2.8	1.6
50	1.2	0.40	3.6	2.8	1.6
60	1.2	0.45	3.6	3.2	3.2
70	1.6	0.77	4.1	4.0	4.0
75		0.89			
80	2.2	0.94	4.3	3.9	4.5
85	2.0	1.0			
90			4.6	4.5	5.3
95		1.1			
100	2.6	1.1	4.6	4.3	5.6

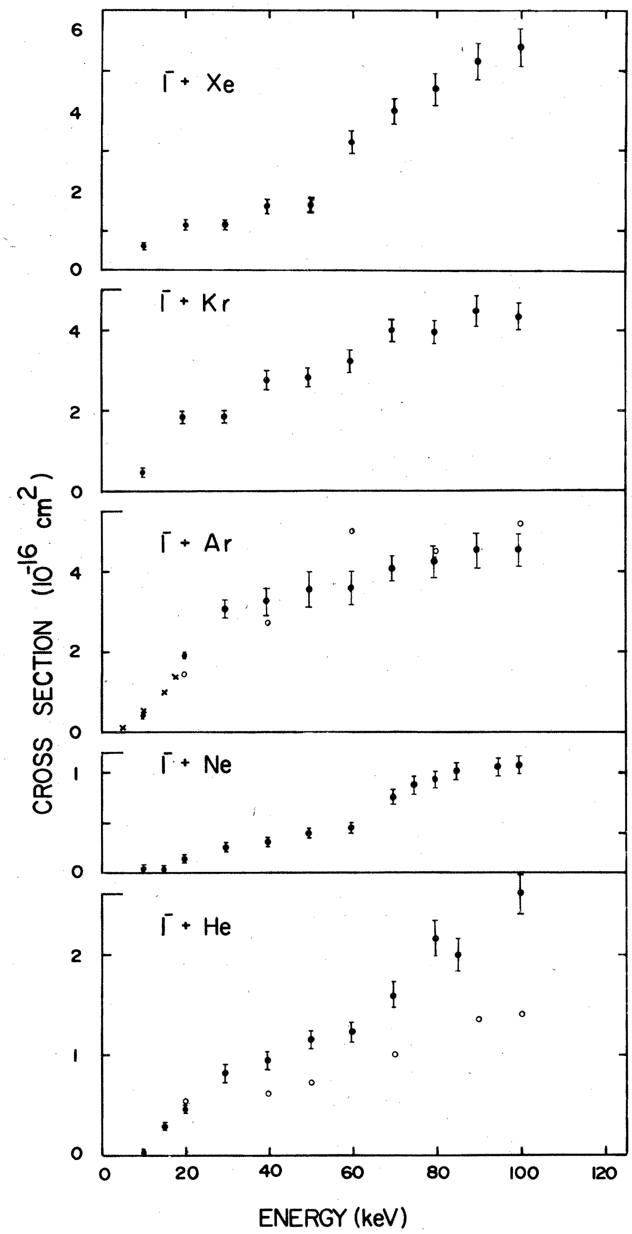

FIG. 2. The cross section for the detachment of two electrons in a single atomic collision. The open circles are the data of Lichtenberg *et al.*,[15] and the crosses are the data of Dukel'skii and Fedorenko.[11] The present data are shown with error bars.

duced. The ionization potential of fluorine is less than that of He and Ne, but more than that of the heavier rare gases so that the low-energy cross sections separate into the two fairly distinct values. Iodine has a smaller ionization potential than all the rare gases so that for the present measurements, preferential target ionization should be less important in reducing the double-electron-detachment cross section and we observe a roughly constant value for all targets at the same center-of-mass energy (see Fig. 2). The double-electron-detachment cross sections from Cl^- show an intermediate behavior between that of F^- and I^- (Hird and Rahman[12]).

Fayeton *et al.*[18] have found evidence in Cl^- + Ar collisions that many of the emitted electrons come from autodetaching double-excited metastable states which decay after the collision. If this process dominates the σ_{-+} cross section then there would be no reason to expect the similarity between the σ_{-+} and the σ_{0+} cross sections. It may possibly account in part for the large double-electron-detachment cross section with the second electron being emitted from the other excited electron state of the doubly excited metastable state.

APPENDIX

The equation for conservation of the total number of particles as they traverse the target is given by

$$\frac{1}{n}\frac{dN^j}{dL}-\sum_{k\,(\neq j)}\sigma_{kj}N^k+\sum_{k\,(\neq j)}\sigma_{jk}N^j=0\ ,$$

where N^j is the number of particles with charge j, and the summations exclude $k=j$. A convenient notation is

$$\sigma_{jj}=\sum_{k\,(\neq j)}\sigma_{jk}\ ,$$

which allows the first equation to be written

$$\frac{1}{n}\frac{dN^j}{dL}-\sum_k\sigma_{kj}N^k=0\ ,$$

where the summation is now over all k.

Neglecting variations of the cross section with energy, the exact solution is a sum of exponential terms. But for targets where σnL is small, these exponentials can be expanded as a power series in nL[24]

$$N^j=a_0+a_1nL+a_2(nL)^2+a_3(nL)^3+\cdots\ ,$$

where $a_0=N_0^j$ is arbitrary and is the initial population of the particles with charge j at the entrance to the target. In the present measurements using a negative-ion beam all the a_0 are zero except when $j=i=-1$.

The differential equation is valid over a range of values of (nL) so that the coefficients of each power of (nL) can be separately set to zero, which gives by successive substitution

$$a_1=N_0^i\sigma_{ij}\ ,$$

$$a_2=\tfrac{1}{2}N_0^i\sum_k\sigma_{ik}\sigma_{kj}\ ,$$

$$a_3=\tfrac{1}{6}N_0^i\sum_{l,k}\sigma_{ik}\sigma_{kl}\sigma_{lj}\ .$$

The apparatus measures the relative populations of the different charge states after the target

$$N=\frac{N^j}{N^i}=\frac{N_0^i\left[\sigma_{ij}(nL)+\frac{1}{2}(nL)^2\sum_k\sigma_{ik}\sigma_{kj}+\cdots\right]}{N_0^i\left[1+\sigma_{ii}(nL)+\frac{1}{2}(nL)^2\sum_k\sigma_{ik}\sigma_{ki}+\cdots\right]}$$

which to first order in (nL) gives

$$\sigma_{ij}=\frac{N}{nL}\left\{1+(nL)\left[\sigma_{ii}-\left[\sum_k\sigma_{ik}\sigma_{kj}\right]\Big/(2\sigma_{ij})\right]\right\}.$$

Extracting from the summation the terms with $k=i$ and $k=j$, and substituting for σ_{jj} and σ_{ii}, the cross section becomes

$$\sigma_{ij}=\frac{N}{nL}\left[1+\frac{nL}{2}\left\{-\left[\left[\sum_{k\,(\neq j)}\sigma_{ik}\right]+\sigma_{ij}\right]+\left[\left[\sum_{k\,(\neq i)}\sigma_{jk}\right]+\sigma_{ji}\right]-\left[\sum_{\substack{k\\k\neq i,k\neq j}}\sigma_{ik}\sigma_{kj}\right]\Big/\sigma_{ij}\right\}\right],$$

where the summations now exclude $k=i$ and $k=j$. Rearrangement gives

$$\sigma_{ij}(1+N/2)=\frac{N}{nL}\left\{1+\frac{nL}{2}\left[\sigma_{ji}+\sum_{\substack{k\\k\neq i,\ k\neq j}}\left[\sigma_{jk}-\sigma_{ik}-\frac{\sigma_{ik}\sigma_{kj}}{\sigma_{ij}}\right]\right]\right\},$$

which provides the relation for σ_{ij} in terms of the ratio of the counts, the target thickness, and the first-order corrections for double collisions of the same particle as it traverses the target.

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