Statistical energy distribution model for the decay of hollow atoms formed in collisions of slow ($v<1$ a.u.) highly charged ions and C_{60}

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It is now well known that electron-capture processes in high impact parameter collisions between slow highly charged ions and clusters (as C_{60} for instance) or surfaces populate high Rydberg levels of the projectile forming a so-called ''hollow atom.'' We present in this paper a statistical energy distribution (SED) model for the analysis of the decay of such hollow atoms. The overbarrier model is employed to estimate the initial binding energy of captured electrons and total geometrical cross sections. We show that although the model firstly derived by Russek was incomplete, a simple modification to it that accounts for hollow atom specifications leads to a better agreement with experimental cross sections over a wide range of projectile ions of different atomic numbers (Ar, Kr, Xe) and different charge states ($q=16-30$). We present also a quantum-mechanics-based formulation of a SED model that allows us to reproduce rather nicely experimental cross sections too. The presented model applied better for high projectile charge states allowing the capture of a great number of electrons that populate a quasicontinuum of Rydberg states for which we do not have to take into account individual Auger transitions.

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INTRODUCTION

In the past decade, a great interest came on hollow atoms as they are formed in slow highly charged ions (SHCI)–surface collision experiments in which they are responsible for a strong secondary electron emission [1]. Later collision experiments of SHCI with clusters such as C_{60} turned out to produce hollow atoms as well [2,3]. For large impact parameter collisions, hollow atom states have sufficiently long lifetimes (>a few tens of fs) to consider that they decay freely in the postcollisionnal part of the projectile trajectory, the interaction with the receding ionized target being completely negligible. This kind of process is referred to as ''atomlike'' collisions in previous works in opposition to ''surfacelike'' or ''solidlike'' collisions that occur at smaller impact parameters.

For atomlike collisions, the initial population on individual shells due to resonantly captured electrons on the projectile can be estimated by the overbarrier model (OBM) [4–7]. Thus, projectile ionization processes could be described by a cascade of Auger transitions between well identified shells. Some attempts to follow the complete Auger cascade of multiply excited ions produced in SHCI-atom or surface collisions have been made for few active electrons [8,9]. Such a method requires a lot of atomic data, such as the binding energy and Auger lifetime of all possible intermediate states. A scaling law of Auger lifetime based on *ab initio* calculations for multiexcited configurations with n electrons in the same shell has first been proposed [10]. This evaluation of Auger relaxation of multiexcited states has been later combined with the overbarrier capture model and a Monte Carlo sampling of ion trajectories in order to investigate the dynamic neutralization and relaxation of SHCI reflected on metal surfaces [11]. Recently, more accurate density functional theory (DFT) calculations of lifetimes of a few hollow configurations of Pb^{20+} and neutral Xe with 20 electrons in $n=7$, 10, or 14 shells have been completed [12]. Nevertheless, when the number of captured electrons becomes too large, following the complete Auger cascade requires a computational effort that is out of reach at the present time.

In this work, we attempt to apply a statistical energy distribution (SED) model to the relaxation of hollow atoms, originally designed by Russek [13] and Russek and Meli [14] to describe the postcollisionnal electronic relaxation of the target in fast singly charged ion-atom collisions. Such a model has also been employed more recently to estimate target final ionization state cross sections in fast (~1 MeV/amu) ion-atom [15], ion-molecule [16], and ion-C_{60} [17] collisions. In this case the local density approximation (LDA) is employed to estimate the amount of energy deposited by the projectile into the target electronic cloud, relaxation of which occurs when the collision partners are completely separated. The transferred energy is then supposed to be statistically distributed among all electrons of the most external shell of the target. We consider here that the decay of a free hollow atom produced in high impact parameter SHCI-C_{60} collisions is a similar problem except that the excitation energy, which originates from electron capture, is distributed among all captured electrons and that the hollow atom may or may not be neutral when the relaxation processes start. The first section of the paper is dedicated to a rapid description of the Russek SED model and to the necessary modification we brought to it in order to take into account the specificity of Auger processes in hollow atom decay. We also recall in this section the basic relations of the Russek-Meli SED model. In the discussion section, we compare theoretical results with previous experimental data.

Model

We consider here the following collision processes at a sufficiently high impact parameter in order to consider that capture and relaxation processes are separated in time,

$$A^{q+}+C_{60}\rightarrow A^{(q-r)+*}+C_{60}^{r+*}\rightarrow A^{(q-s)+}+ne^{-}+C_{60}^{r+*}.$$

Electronic or vibration relaxation of the excited target is beyond the scope of the present paper (for instance, see [18,19]). We only consider here the deexcitation of the projectile as an independent process from the capture process. The binding energy of each captured electron, E_i^C, can be estimated from the OBM [5–7]. Then the total excitation energy for r captured electrons is $E_r=\Sigma_{i=1}^{r}(I_{q-i+1}^{P}-E_i^C)$, where I_k^P is the kth ionization potential of the projectile. It can, however, be remarked that for HCI the summation over the ionization potentials is much greater than the sum of the binding energies, so that in zeroth order of approximation we could write $E_r\approx\Sigma_{i=1}^{r}I_{q-i+1}^{P}$, but we use in the first order of approximation $E_r\approx\Sigma_{i=1}^{r}(I_{q-i+1}^{P}-I_i^T)$, where I_i^T is the ith ionization potential of the target, which is estimated to $I_i^T\approx 3i+4$ eV according to a fit from the data of paper [20]. The OBM is also employed to estimate total cross sections σ_r, i.e., the cross sections for having r active electrons during the collision. By determining the critical overbarrier distance, R_r, at which the rth electron can be transferred to the projectile, we obtain geometrical cross sections: $\sigma_r=\pi(R_r^2-R_{r+1}^2)$.

Knowing the excitation energy E_r, the probability $P_r^n(E_r)$ that n electrons and only n can escape from the projectile potential well can be estimated with the SED model. Together with σ_r, a theoretical estimation of σ_r^s can be obtained for comparison with experimental data. The expression of $P_r^n(E_r)$ can be derived in the three following different ways: (1) Appendix A of Russek's paper of 1963 [13]; (2) Appendix A of Ref. [13] together with an energy criterion on the kinetic energy of ionized electrons; and (3) from the paper of 1970 Russek and Meli [14].

(1) $P_r^n(E_r)$ is defined as the probability that when excitation energy E_r is distributed among the r active electrons, n and only n have enough energy to escape. This is given by the limit as $\varepsilon\rightarrow 0$ of the number of ways in which $m=\{E_r/\varepsilon\}$ (curly brackets mean integral part) units of energy can be distributed among r electrons such that n and only n electrons have more than w_r^n units of energy, divided by the total number of ways to distribute m units of energy among the r electrons. In the staggered ionization case,

$$w_r^n=\left\{\left(\sum_{i=1}^{n}I_{q-r+i}^{p}\right)\Big/\,n\right\}$$

is the quantified mean energy needed to remove n electrons from the projectile. Now, it can be easily shown [Eq. (A16) of Ref. [13]]:

$$P_r^n(m)=\frac{1}{K_r(m)}\binom{r}{n}\sum_{j=0}^{m-nw_r^n}K_n(j)Q_{r-n}^{w_r^{n+1}}(m-nw_r^n-j), \tag{1}$$

where

$$K_a(b)=\binom{a+b-1}{b}$$

is the number of ways to distribute b units of energy on "a" electrons and $Q_{r-n}^{w_r^{n+1}}(m-nw_r^n-j)$ is the number of ways to distribute the $m-nw_r^n-j$ units of remaining energy on the $(r-n)$ remaining electrons such that each remaining electron has less than w_r^{n+1} units of energy. The function $Q_a^c(b)$ is given by

$$Q_a^c(b)=\sum_{i=0}^{\{b/c\}}(-1)^i\binom{a}{i}K_a(b-ic).$$

Though it is possible to derive a simpler expression for Eq. (1) by going to the limit $\varepsilon\rightarrow 0$, we chose to compute those discrete expressions keeping in mind that the relative error is less than 1% when ε is increased from 0.01 to 1.

(2) In this purely phenomenological model described above, all the kinetic energy cells are equiprobable for the ejected electron. In fact, it is well known that the Auger process is a binary electron-electron interaction which only allows for an electron to be ejected with a characteristic kinetic energy that corresponds to the difference of binding energy of final and initial atomic state of the remaining electron, giving rise to well defined lines in the energy spectrum of autoionized electrons. Nevertheless, for hollow atoms the "shake-off" process, i.e., the multielectron interaction between the ejected electron and other bound electrons can lower the ejected electron kinetic energy and blur the spectrum. In order to take into account the previous remarks we introduce in the statistical model a criterion for the kinetic energy of ejected electrons: we consider that two electrons cannot exchange more than the mean excitation energy E_r/r so that the maximum kinetic energy for an ejected electron cannot exceed $E_{kr}^{\max}=pE_r/r$, where p is a parameter such that $0<p\leqslant 1$. Then, from Eq. (1) the K functions have to be replaced by appropriate Q functions:

$$P_r^n(m)=\frac{1}{Q_r^{u_r}(m)}\binom{r}{n}\sum_{j=0}^{m-nw_r^n}Q_n^{u_r}(j)Q_{r-n}^{w_r^{n+1}}(m-nw_r^n-j) \tag{2}$$

with $u_r=\{E_{kr}^{\max}/\varepsilon\}$.

(3) In Ref. [14] the previous model is criticized and quantum mechanics is introduced. It is pointed out that if some energy remains on the residual ion, it must be stable against further autoionization processes. In consequence it is stated that the residual ion must be at most singly excited after the ionization process is over. However, in the case of highly charged ions, the situation may be more complex in the way that it has been previously demonstrated in studies of doubly and triply excited ions that when Rydberg states can be populated, the stabilization of all excited electrons is also possible by photon emission [21,22]. Nevertheless, we are going to apply, according to Ref. [14], the restriction to the statistical model that the final state of residual ion is at most monoexcited. A second assumption in the model is to suppose equal

probability per unit of volume in momentum phase space, allowing us thus to derive the following quantum-mechanics based relation:

$$P_n^r(E_k) = \frac{\binom{r}{n} g^n S_n\left(\frac{E_k}{I_i^p}\right)}{\sum_{i=1}^{r} \binom{r}{i} g^i S_i\left(\frac{E_k}{I_i^p}\right)}. \quad (3)$$

The g factor contains the quantum mechanical part of the model and is related to mean square matrix elements of interaction between the initial state and all final states in which n electrons are ionized. As g is out of reach of any present calculation, it is considered as an adjustable parameter. E_k is the total kinetic energy of ejected electrons determined by $E_k = E_r - \Sigma_{i=1}^{n} I_{q-r+i}^p - E_{\text{res}}$. Accordingly to [14] and [15], the excitation energy of residual ion E_{res} has been set to 0 for the results presented below. Setting E_{res} to nonzero values leads to the ejection of fewer electrons, which can be compensated for by increasing the value of g. Function S_n arises with the derivation of the density of final states (see the Appendix in Ref. [14]):

$$S_n(E_k) = \frac{2^{\{(n-1)/2\}} \pi^{\{n/2\}} E_k^{(3n-2)/2}}{(3n-2)!!}.$$

RESULTS AND DISCUSSION

$Xe^{30+} - C_{60}$ collisions have been extensively studied in previous works [23–25] and have been chosen as a test system for the models. Figure 1(a) shows fits of experimental σ_r^s cross sections and Figs. 1(b) to 1(d) show theoretical results obtained with Eqs. (1), (2), and (3), respectively. The agreement between model (1) and experiment is rather poor: the theoretical σ_r^s curves are found to be too narrow and shifted towards low r values. For model (2), the agreement with experimental cross sections is already much better with parameter $p=1$ (i.e., without an adjustable parameter). However, the best agreement with experimental results has been found for $p=0.7$ as shown in Fig. 1(c). This is consistent with the experimental finding that 80% of ejected electrons have energies less than 100 eV [24]. Nevertheless, the theoretical curves are found narrower than the experimental curves but the centers of distributions are well reproduced. Figure 1(d) has been obtained with model (3) with $g=1$; the agreement is not as good as with model (2), especially for the width of the curves. As defined in the preceding section, the factor g contains the matrix elements between initial and final states. In fact, for each value of r, different initial configurations are populated and consequently g should take different values for different r values. For $Xe^{30+} - C_{60}$ with $r=27$, Fig. 2 demonstrates the effect of the g parameter on P_n^r curves. Increasing g leads to an increase of the mean number of ejected electrons and to narrower distributions. The best agreement with experiment is obtained for $g=30$. An optimization procedure has been employed to determine the g value that allows us to fit each P_n^r experimental curve. Figure 3(a) displays the results obtained for the theoretical σ_r^s cross

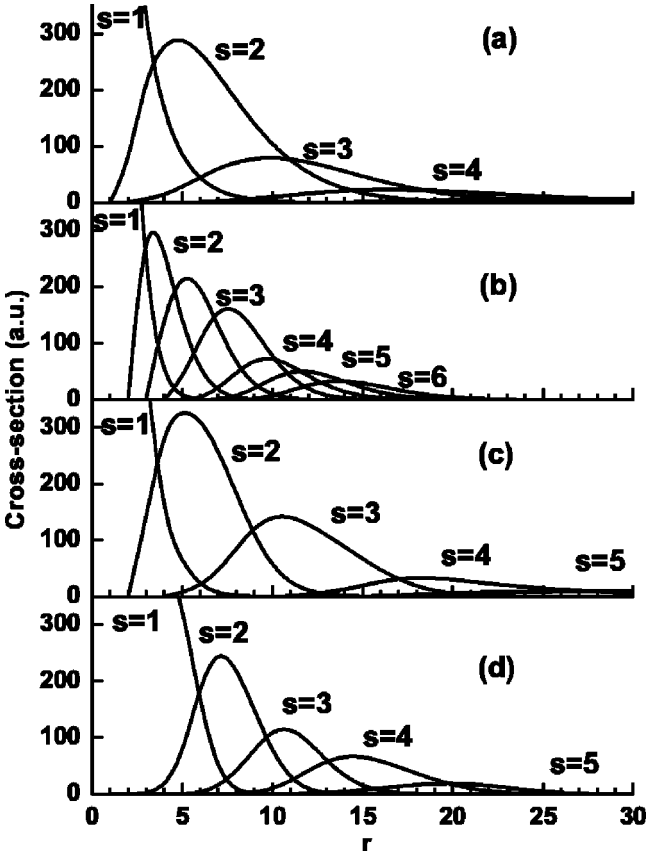

FIG. 1. (a) Experimental cross sections σ_r^s for Xe^{30+}-C_{60} collisions for $s=1-4$ corresponding to outside C_{60} cage collisions. (b), (c), and (d) Theoretical σ_r^s cross sections calculated with original Russek's SED, with modified Russek's model (parameter $p=0.7$) and with the model of Russek and Meli model (parameter $g=300$ for all r values), respectively. A better agreement between theory and experiment is obtained for models (2) and (3).

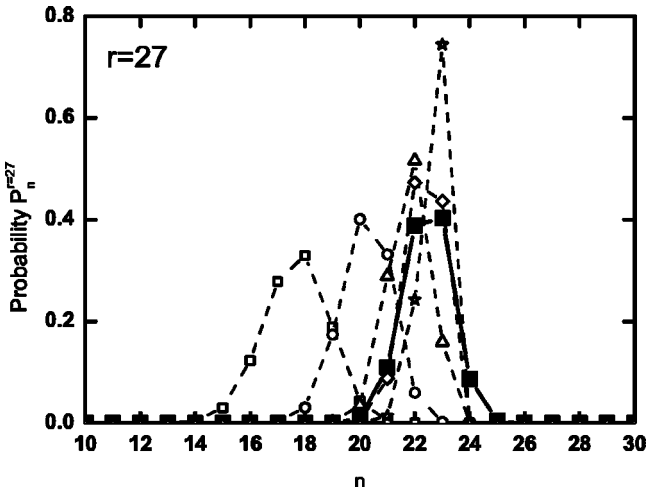

FIG. 2. Experimental (filled squares) and calculated probabilities of the ejection of n electrons from r captured electrons (P_n^r) for $Xe^{30+} - C_{60}$ collisions employing $g=0.1$ (empty squares), $g=1$ (circles), $g=10$ (triangles), $g=30$ (diamonds—same value as Fig. 1), and $g=100$ (stars). Lines are to guide the eyes.

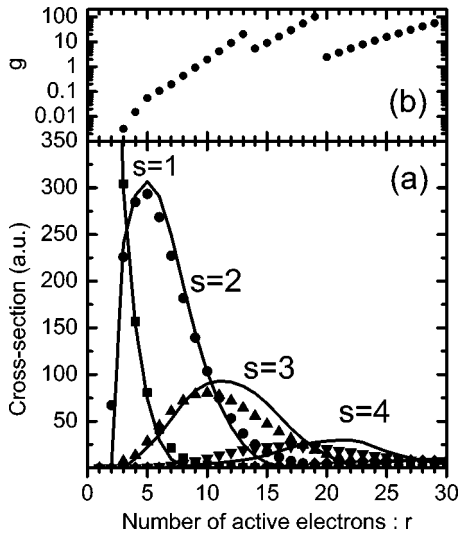

FIG. 3. (a) Experimental σ_r^s for $Xe^{30+}-C_{60}$ (squares: $s=1$; circles: $s=2$; up triangles: $s=3$; down triangles: $s=4$) versus the number of active electrons. Lines: theoretical σ_r^s for $Xe^{30+}-C_{60}$ calculated with model (3) in which g has been adjusted for each r value in order to fit the experimental P_n^r distributions. (b) Corresponding g values obtained in the fitting procedure.

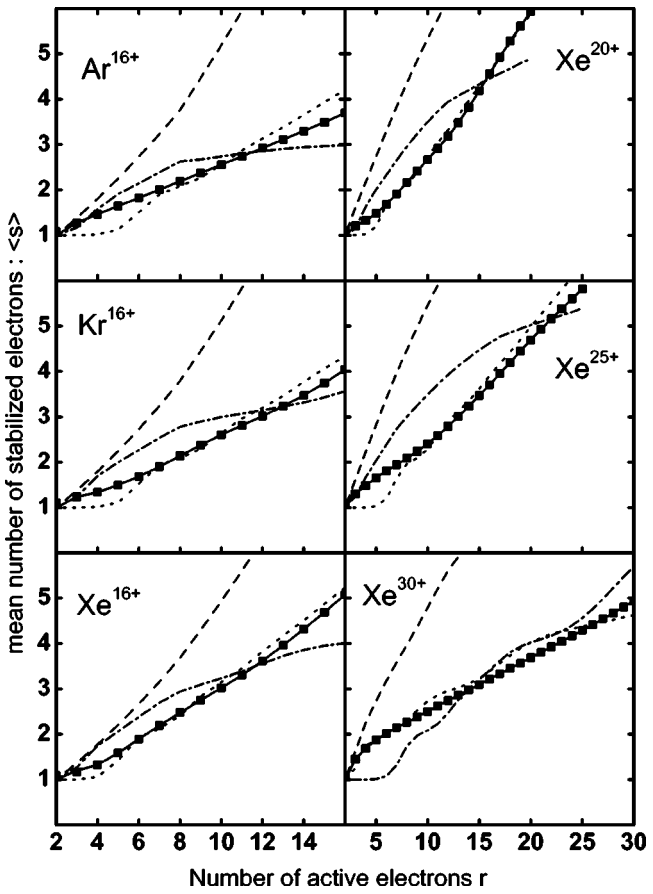

FIG. 4. Filled squares: experimental mean value of s obtained from σ_r^s cross-section measurements. Dashed, dash-dotted, and dotted lines are theoretical mean s values calculated with models (1), (2), and (3), respectively. For model (2), the best agreement with experimental data has been found for parameter $p=0.7$ for Ar^{16+} and Xe^{30+} and $p=0.8$ for the other ions. For model (3), the same value of the g parameter has been taken for all r values and the best agreement with experimental curves has been found for $g=17$, 17, 7, 7, 23, 15 for Ar^{16+}, Kr^{16+}, Xe^{16+}, Xe^{20+}, Xe^{25+}, respectively. Solid lines have been obtained using model (3) and adjusting the g parameter for each r value such that the theoretical mean number of ejected electrons matches with experiment (like in Figs. 2 and 3).

sections and the comparison with experimental data shows a rather nice agreement. The variation of g versus r [Fig. 3(b)] is found to be dominantly an exponential increase, except two discontinuities at $r=14$ and $r=20$ that "technically" arise in the fitting process and for which no physical meaning has been found yet. The overall increase of g (related to mean square matrix elements) versus r shows that the probability P_n^r is not simply given by the ratio of the density of final states as in the $g=1$ case. The OBM shows that electrons are captured in more and more bound levels as r increases. Consequently, the mean excitation energy E_r/r and so the mean kinetic energy of ejected electrons decreases as r increases. So, the obtained mean square matrix elements increasing versus decreasing kinetic energy of ejected electrons is coherent with the well known fact that higher probabilities are expected for autoionization channels near threshold.

Figure 4 shows experimental and theoretical values using relations (1), (2), and (3) of the mean number of stabilized electrons ($\langle s\rangle = r - \langle n\rangle$) as a function of r for Ar^{16+}, Kr^{16+}, Xe^{16+}, Xe^{20+}, Xe^{25+}, Xe^{30+} projectiles. For a given value of r, model (1) always overestimates the number of stabilized electrons. This is due to the fact that an electron can be ejected with a high kinetic energy leaving the remaining ion with a low excitation energy that forbids the ejection of a sufficiently high number of electrons. Model (2) solves this inconvenience and a good agreement with experimental data is obtained by setting the parameter p to 0.7 for Ar^{16+} and Xe^{30+}, and 0.8 for the other projectiles. On Fig. 4 are also displayed the $\langle s\rangle$ calculated with model (3) for $g=17$, 17, 7, 7, 23, 15 for Ar^{16+}, Kr^{16+}, Xe^{16+}, Xe^{20+}, Xe^{25+}, respectively. Those values of g were chosen in order to obtain best fits of theoretical curves with experimental curves. It can be remarked that both models (2) and (3) agree rather well with experiment for those six different collision systems though slight discrepancies can be noticed. Model (2) slightly overestimates $\langle s\rangle$ for intermediate r values and underestimate $\langle s\rangle$ for high r values. Model (3) underestimates $\langle s\rangle$ for small active electron numbers, but the agreement is rather nice for $r>5$. Generally, Fig. 4 demonstrates the applicability of the SED model over a wide range of projectile natures and charges. Solid lines in Fig. 4 have been obtained by adjusting g parameters for each value of r in order that theoretical mean numbers of ejected electrons match with experimental ones. However, the fact that it is always possible to match mean values does not mean that experimental cross sections σ_r^s are perfectly reproduced by the model as shown in Fig. 2. We are generally led to set g to higher values than in papers [13–16] where, for the study of target ionization at high velocities, g values are set in the range 0.01 to 1. Small g values indicate that ionization of two (or more) electrons is

much less probable than single ionization. In our case, the potential depth of highly charged ions is much deeper and the total excitation energy is much higher so that we are in the opposite situation where multiple ionizations become more probable than single ionization.

It can be expected that theory overestimates the mean number of ejected electrons, since radiative transitions are completely neglected in the present models. Although autoionization is the main decay process for low multiplicity multiexcited states, it has been demonstrated that doubly and triply excited states with a high multiplicity (quartet, sextet,...) decay mainly by radiative transitions [21,22]. A further improvement of the model could be to introduce the contribution of radiative transitions. A first attempt in this direction can be easily made by setting nonzero values to E_{res} in the estimation of the total ejected electron kinetic energy E_k. For high r values a better agreement with experiment is always obtained with $E_{\mathrm{res}}=0$, though for low r values, it was possible to reproduce experimental P_r^n curves with $g=1$ and $E_{\mathrm{res}}>0$ (for instance, Xe^{30+}, $r=4$, and $g=1$ leads to $E_{\mathrm{res}}=1200$ eV).

CONCLUSION

We have presented three formulations for the SED model and put it together with the OBM model in order to describe multielectron capture and projectile relaxation processes in SHCI-C_{60} collisions. Although an adjustable parameter is always needed to match the mean number of ejected electrons, it is already remarkable that with such a crude model, the shape of σ_r^s curves is rather well reproduced. Though the original Russek SED model does not allow us to reproduce experimental data, the introduction of the energy criterion gives much better results. With the quantum-mechanics-based Russek-Meli formulation we obtained also a nice agreement between theoretical and experimental cross sections. Although a recent investigation on statistical properties of hollow nitrogen employing the very demanding Hartree-Fock configuration-interaction method allowed us to determine the mean value and standard deviation of 237 individual states with five electrons in the $n=4$ shell of nitrogen [26], the virtues of the present OBM-SED model is its great simplicity through which σ_r^s cross sections can be easily estimated and its applicability over a wide range of projectile nature and charge.

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