Modifications of the Impulse Approximation for Ionization and Detachment Cross Sections*

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(Received 1 June 1965)

A bound-state correction is suggested for the Thomson-Gryzinski impulse approximation. Also, it is noted that Slater's rules yield estimates of kinetic-energy expectation values which are more accurate than those used in previous applications of this approximation. These corrections are important for neutral atoms with outer electrons in a p state and for all negative ions. Comparison is made with experiment and previous theoretical results.

I. INTRODUCTION

THE impulse approximation of Thomson[1] with the modifications of Gryzinski[2] allowing for the motion of the bound electrons has provided simple analytic expressions for atomic ionization and excitation cross sections which prove to be more accurate at intermediate energies than the results of much more complicated calculations.[2] The essential assumption of this approximation is that the nucleus has negligible effect on the energy exchange between the bound and scattered particles during the collision, i.e., that the collision may be treated as a simple two-body Coulomb collision as far as the energy exchange is concerned. This approximation in its purest form has been considered by Stabler[3]; Gryzinski has made an additional approximation which in some sense takes into account the fact that the target electron is bound and improves agreement with experiment at intermediate energies. It has been noted that, the classical and quantum Coulomb cross sections being identical, the use of classical language by these authors does not imply a classical approximation.[4]

The impulse approximation yields poor results at threshold where exchange and polarization effects are important and at high energies where the bound state of the scatterer evidently enhances the cross section. Comparison with experiment[2,5,6] has demonstrated that Gryzinski's ionization cross sections agree with experiment to within about 25% over energies ranging from a few electron volts above threshold to about 1000 eV with neon as a notable exception. Previous calculations which indicated poor results for the alkali atoms[7] overlooked the importance of autoionization and inner-shell ionization in the heavy alkalis.

Gryzinski[8] has recently discussed exchange corrections, and by means of unphysical velocity distributions for the bound electrons, obtained the correct high-energy dependence without significantly altering the results of intermediate energies.

This paper will deal with the occasional failure at intermediate energies. A simple modification of Grysinski's cross sections will be proposed to allow for the bound nature of the target electron at intermediate energies and Slater's rules[9] will be used to estimate the expectation value of the kinetic energy of the bound electron in contrast to many previous applications where the kinetic energy has been assumed to be equal to the ionization potential. These corrections are important for neutral atoms whose outer electrons are in a p state and are particularly important for detachment from negative ions.

II. THE IMPULSE APPROXIMATION

Following Gryzinski,[2] we have for the change in energy of particle 2 in a two-electron Coulomb collision,

$$\Delta E_2 = \frac{E_1 - E_2 + 2\lambda (E_1 E_2)^{1/2} \sin\theta \cos\alpha}{1+\lambda^2}, \qquad (1)$$

where

$$\lambda = (mV^2/2e^2)s,$$

E_1 and E_2 are the particle energies, s is the impact parameter, θ is the angle between the velocity vectors, α is the aximuthal angle between the plane of $\mathbf{v}_1$ and $\mathbf{v}_2$ and the plane in which the collision occurs in the center-of-mass frame, and V is the relative velocity.

If we designate the colliding electron as particle 2 and the bound electron as particle 1, the cross section

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* The research reported in this paper was sponsored by the National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, Maryland, under Contract No. NAS5-3649.

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[8] M. Gryzinski, Phys. Rev. **138**, A336 (1965).
[9] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I, Chap. 15, p. 369.

for ionization is given by[2]

$$\sigma_I(E_2)=\int_0^\infty N(E_1)dE_1\int_U^{E_2} d|\Delta E_2| \times\int_{-1}^{1} d\cos\theta\frac{V}{v_2}\int_0^\infty \left|\frac{d\Delta E_2}{d\alpha}\right|^{-1} s\,ds, \quad (2)$$

where U is the ionization potential. The function $N(E_1)$ is the kinetic-energy distribution of the bound electron which throughout the remainder of this paper will be taken to be $\delta(E_1-\bar{E}_1)$ where $\bar{E}_1$ is the expectation value of the kinetic energy. The s integration yields

$$\sigma_I(E_2)=\frac{\pi e^4}{E_2^{1/2}}\int_U^{E_2} d|\Delta E_2| \times\int_{-1}^{+1} d\cos\theta\frac{1}{(E_1+E_2-2E_1E_2\cos\theta)^{3/2}} \times\left\{\frac{2E_1E_2\sin^2\theta}{\Delta E_2^3}-\frac{(E_2E_1)}{\Delta E_2^2}\right\}. \quad (3)$$

The remaining integrations have been performed exactly by Stabler.[3] In order to expedite the θ integration, Gryzinski[2] replaced the $(E_1+E_2-2E_1E_2\cos\theta)^{3/2}$ factor in the denominator by $(E_1+E_2)^{3/2}$ yielding approximate results which are actually slightly more complicated than Stabler's exact results, but give better agreement with experiment. The exact theory yields large cross sections. Gryzinski's approximation yields

$$\sigma_G=4\pi a_0^2\left(\frac{R_y}{U}\right)^2\frac{2}{3}\frac{1}{E_2E_1^{1/2}}\left(\frac{E_1+U}{E_1+E_2}\right)^{3/2}[E_2-U]^{3/2} \quad U<E_2<U+E_1,$$

$$\sigma_G=4\pi a_0^2\left(\frac{R_y}{U}\right)^2\left[\frac{E_2}{E_1+E_2}\right]^{3/2} \times\left\{\frac{[\frac{2}{3}E_1+U]}{E_2}-\frac{[UE_1+U^2]}{E_2^2}\right\} \quad U+E_1<E_2, \quad (4)$$

where a_0 is the Bohr radius and R_y is a Rydberg (13.6 eV).

III. THE KINETIC ENERGY

All theories based on the impulse approximation, Eq. (2), require the expectation value of the kinetic energy of the bound electron. In previous applications, with the exception of helium where one may directly invoke the virial theorem, the kinetic energy was assumed to be equal to the ionization potential. Slater[9] has suggested a simple set of rules for estimating this kinetic energy. Since Slater's rules have provided good estimates of the total energy of atomic configurations, they would seem to provide a better approach to the kinetic energy than the ionization potential. Briefly, the kinetic energy of an electron in atomic state (n,l) is approximately

$$E_1\simeq(Z_{\text{eff}}/n^*)^2R_y, \quad (5)$$

where

$$Z_{\text{eff}}=Z-\sum_{\eta=1}^{n-1}\sum_{\lambda=0}^{\eta-1}N(\eta,\lambda)-0.35[N(n,l)-1] +\delta_{l,0}\{0.15\sum_{\lambda=0}^{n-2}N(n-1,\lambda)-0.35N(n,l+1) +0.05\delta_{n,0}[N(n,l)-1]\} +\delta_{l,1}\{0.15\sum_{\lambda=0}^{n-2}N(n-1,\lambda)-0.35N(n,l-1)\}, \quad (6)$$

Z is the nuclear charge, $\delta_{a,b}$ is the Kroneker delta symbol, $N(\eta,\lambda)$ is the number of electrons with quantum numbers $n=\eta$ and $l=\lambda$, and n^* takes on the values 1, 2, 3, 3.7, 4, and 4.2 corresponding to actual quantum numbers n equal to 1, 2, 3, 4, 5, and 6, respectively.

Applying Eq. (6) to the outer electrons of neutral atoms, one discovers that the ratio of the kinetic energy to the ionization potential exceeds two for all atoms with outer electrons in a p state, increases with the number of p-state electrons involved, and obtains a value of order five for the inert gases. Thus the ionization potential is a poor approximation for the kinetic energy of these atoms. The values of E_1/U for the negative ions H^-, C^-, O^-, F^-, S^-, Cl^-, B_r^-, and I^-, are 9.6, 25.3, 40.6, 22.1, 19.0, 13.1, 14.8, and 13.9, respectively.

In Fig. 1, $(\sigma_I/4\pi a_0^2)(U/R_y)^2$, based on Eq. (4), is plotted as a function of E_2/U for various values of

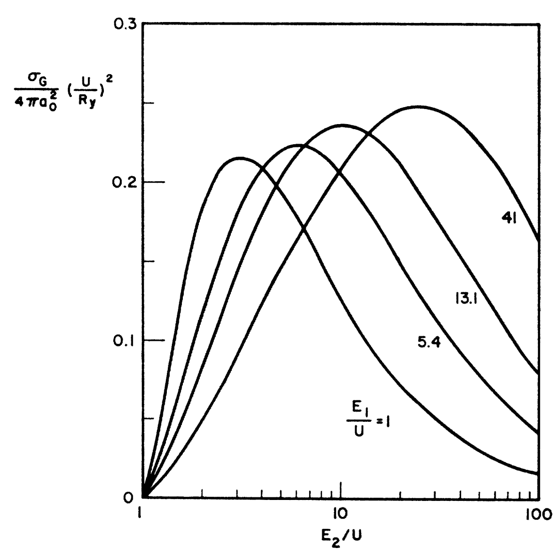

FIG. 1. Effect of the bound-state kinetic energy on the shape of the ionization-cross-section curve. E_1 is the bound-state energy, E_2 is the energy of the bombarding particle, U is the ionization potential, and σ_G is the ionization cross section.

E_1/U. Although the value of the maximum is essentially independent of E_1/U, it becomes broader and its position is displaced to higher energies as E_1/U increases. The maximum occurs approximately at

$$E_2/U=\tfrac{5}{2}+0.68(E_1/U),\qquad 1<E_1/U<5$$

$$E_2/U=\tfrac{13}{4}+0.52(E_1/U,\qquad 5<E_1U.$$

IV. BOUND-STATE CORRECTIONS

One obvious correction to the simple two-body-collision approximation is to decrease the contribution of collisions which occur in times large compared to the period of the bound electron in a manner reminiscent of the Bohr energy loss formula.[10]

Classical concepts will be used to obtain estimates of such a correction. One should only count collisions for which

$$\frac{s}{V}<\frac{a}{(2E_1/m)^{1/2}}\,, \tag{7}$$

where s is the impact parameter, V is the relative velocity, and a is the shell radius. Estimates of a may be obtained from Hartree-Foch calculations when available; or, one may use Slater's rules

$$a\simeq n^{*2}a_0/Z_{\mathrm{eff}}=n^*a_0(R_y/E_1)^{1/2}. \tag{8}$$

Thus, a condition

$$\lambda<\lambda m \tag{9}$$

is required, where

$$\lambda\equiv(E_1+E_2-2(E_1E_2)^{1/2}\cos\theta)s(e^2)^{-1}$$

and

$$\lambda_m=\frac{n^*}{2R_y^{1/2}}\frac{(E_1+E_2-2(E_1E_2)^{1/2}\cos\theta)^{3/2}}{E_1}.$$

In order to impose this condition correctly, one should cut off the integration over impact parameter in Eq. (2); however, the resulting loss of symmetry complicates the θ and ΔE_2 integration considerably. In order to obtain estimates of the nature of the corrections, we shall integrate over all impact parameters and consider the effect of condition (9) on the θ and $|\Delta E_2|$ integrations.

Since we are interested in corrections at intermediate energies, Eq. (1) will be considered in the region $E_2\simeq E_1+U$, where

$$\Delta E_2\simeq\frac{-U-2\lambda(E_1^2+E_1U)^{1/2}}{1+\lambda^2}. \tag{10}$$

A rough plot of ΔE_2 versus λ is given in Fig. 2.

Inspection of Eqs. (2) and (3) reveals that major contributions to the cross section come from collisions with $\Delta E_2\simeq -U$ and, other things being equal, collisions with large impact parameters.

When the collision parameters are such that

$$\lambda_m\ll 1\,, \tag{11}$$

the contributions to the cross section must be discounted simply because most of the collisions with $|\Delta E_2|\geq U$ are forbidden. It would be desirable to impose such a reduction by introducing a cutoff in the θ integration; but, once again, the integration becomes difficult. Gryzinski's ansatz prior to the θ integration is certainly a correction in the direction required; but it is difficult to see *a priori* that it is equivalent to such a cutoff. Nevertheless, using the success of the resulting cross section for many atoms as justification, we shall accept his ansatz.

The point of this section is that even when $\lambda_m>1$ a further correction may be required by inequality (9). A large contribution to the cross section occurs for λ in the region designated as λ_U in Fig. 2; for in this re-

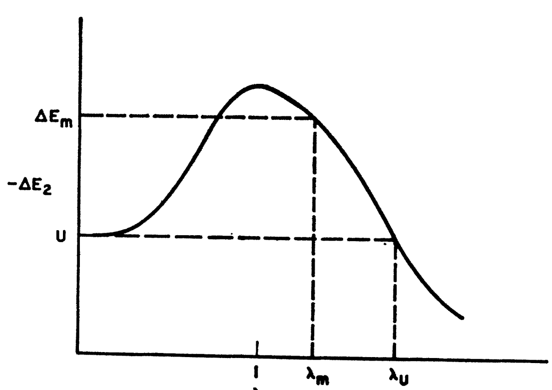

FIG. 2. Typical variation of the energy exchanged as a function of impact parameter. $|\Delta E_2|$ is the energy exchanged and $\lambda\equiv\frac{1}{2}(mV^2/e^2)s$, where V is the relative velocity and s is the impact parameter.

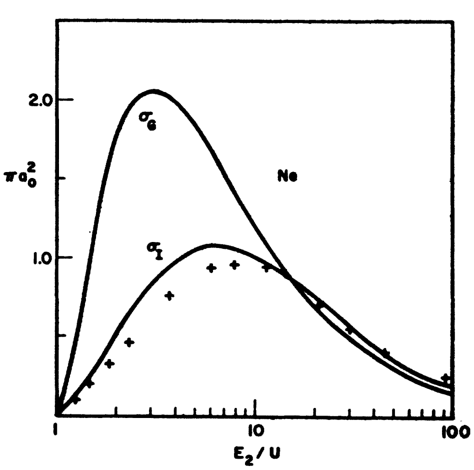

FIG. 3. Ionization cross section of Ne, ($U=21.6$ eV). σ_G is the uncorrected cross section with $E_1=U$ and σ_I is the corrected impulse approximation with E_1 estimated by Slater's rules. Plus signs denote experiment.

[10] E. Fermi, *Nuclear Physics* (University of Chicago Press, Chicago, 1949), Chap. II, p. 27.

gion we have both $|\Delta E_2|\simeq U$ and a large impact parameter. If $\lambda_m<\lambda_U$, the contribution of this region must be discounted; that is to say if

$$\lambda_m\simeq\frac{n^*(2E_1+U)^{3/2}}{2R_y^{1/2}E_1} \tag{12}$$

is substituted into Eq. (10) and the resulting ΔE_2 is less than $-U$,

$$\Delta E_2(\lambda_m)\equiv-\Delta E_m<-U\,, \tag{13}$$

then a further bound-state correction should be applied to the cross section. This correction could be approximated by changing the lower limit of integration of $|\Delta E_2|$ from U to ΔE_m. Since this correction is only important in atoms for which $E_1\gg U$, this is equivalent to replacing the factor $1/U^2$ in expression (4) by $1/\Delta E_m^2$. This suggests that Gryzinski's cross section for intermediate energies should be replaced by

$$\sigma_I=4\pi a_0^2\left(\frac{R_y}{W}\right)^2\frac{2}{3}\frac{1}{E_2E_1^{1/2}}\left(\frac{E_1+U}{E_1+E_2}\right)^{3/2}[E_2-U]^{3/2}\qquad U<E_2<U+E_1\,,$$

$$\sigma_I=4\pi a_0^2\left(\frac{R_y}{W}\right)^2\left[\frac{E_2}{E_1+E_2}\right]^{3/2}\left[\frac{\frac{2}{3}E_1+U}{E_2}-\frac{UE_1+U^2}{E_2^2}\right]\qquad U+E_1<E_2\,, \tag{14}$$

where

$$W=U,\quad U>\Delta E_m\,,$$
$$=\Delta E_m\quad U<\Delta E_m\,.$$

These cross sections should only be reliable for $E_2\gg\Delta E_m$.

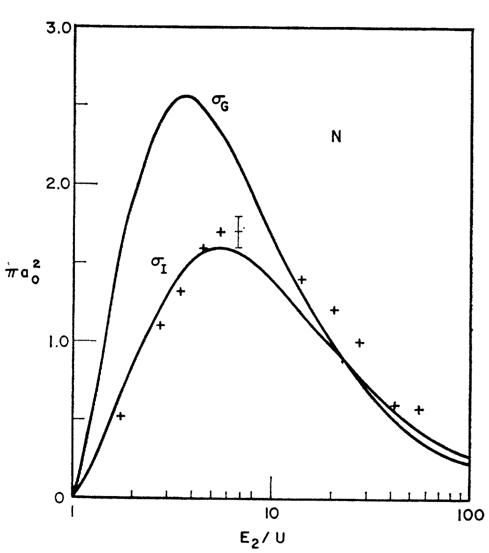

FIG. 4. Ionization cross section of N ($U=14.5$ eV). σ_G is the uncorrected cross section with $E_1=U$ and σ_I is the corrected impulse approximation with E_1 estimated by Slater's rules. Plus signs denote experiment.

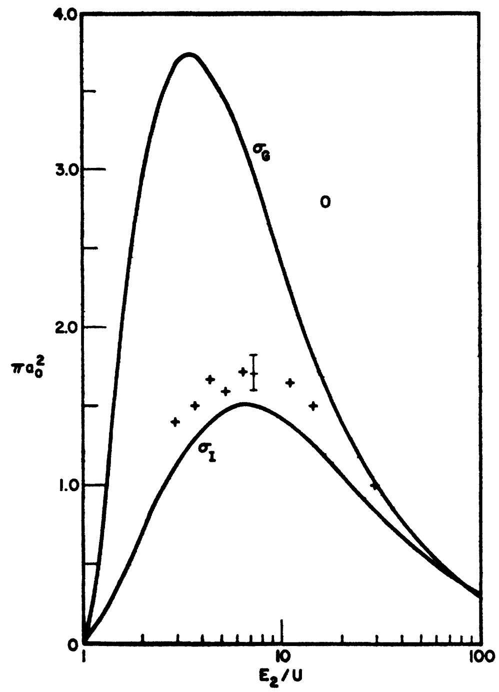

FIG. 5. Ionization cross section of O ($U=13.6$ eV). σ_G is the uncorrected cross section with $E_1=U$ and σ_I is the corrected impulse approximation with E_1 estimated by Slater's rules. Plus signs denote experiment.

V. APPLICATION

The only atom considered previously for which $\Delta E_m>U$ is neon which was a notable exception to the success of the previous theory. Experimental data exist for nitrogen and oxygen for which $\Delta E_m>U$. In argon, $\Delta E_m<U$, so the results of Sec. IV are not pertinent; however, the kinetic-energy considerations of Sec. III should be important. In Figs. 3, 4, 5, and 6,

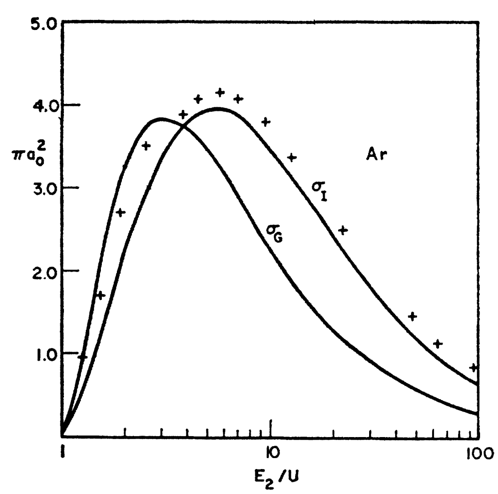

FIG. 6. Ionization cross section of Ar ($U=15.8$ eV). σ_G is the uncorrected cross section with $E_1=U$ and σ_I is the corrected impulse approximation with E_1 estimated by Slater's rules. Plus signs denote experiment.

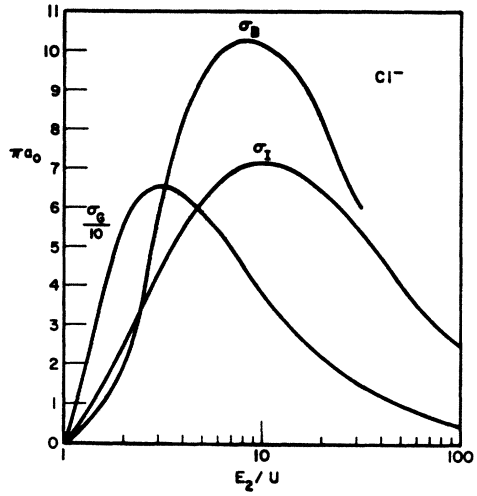

FIG. 7. Ionization cross section of Cl^- ($U=3.8$ eV). σ_G is the uncorrected cross section with $E_1=U$, σ_I is the corrected impulse approximation with E_1 estimated by Slater's rules, and σ_B is the Born approximation.

we have compared the cross sections in Eq. (14) to those of Gryzinski without the above corrections and experiment[11–13] for Ne, N, O, and Ar, respectively. Since the impact theory outlined above predicts the probability of ionizing the given electron regardless of subsequent ionization performed by the colliding particle, comparisons have been made to total ionization cross sections. Ionization of the *s* shell is significant in O and N.

The above corrections are particularly important for negative ions. Massey and Smith[14] have calculated the detachment cross section of Cl^- using the Born approximation. A comparison is made in Fig. 7. A check at high energies, where the Bethe-Born approximation[15] should be valid, indicates that they omitted a factor of 6 for the number of *p* electrons so that six times their cross section has been used.

The only other negative ion for which calculations have been made is H^-. In this case, the quantity ΔE_m is not only larger than the ionization potential, but is also larger than the kinetic energy of the bound electron, indicating that even at intermediate energies much of the contribution for the cross section comes from collisions with collision times larger than the period of the bound electron; hence, the impulse approximation seems a very poor one for this ion.

VI. CONCLUSION

Although the success of the cross section given by Eq. (14) over a wide range of energies indicates their usefulness as semiempirical expressions, it should not overshadow the crudeness of the corrections involved. We have accepted Gryzinski's ansatz with only slight justification and the additional correction derived in Sec. IV was based on arguments applicable to the immediate vicinity of the maximum cross section. The success over a wide energy range seems fortuitous; however, this success emphasizes the desirability of applying similar bound-state corrections to the impulse approximation in a more systematic fashion.

The need for Slater's rules for estimating kinetic energies seems clearly established.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. Robert C. Stabler for many helpful discussions and Dr. Wolfgang Zernik for many useful comments on the manuscript.

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