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Behavior of the Ionization Cross Section in Collisions of High-Energy Electrons With Hydrogenic Atoms

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The ionization cross section per unit range of the energy ϵ of the ejected electrons for collision of an incident charged particle of high energy E with an atomic system is given by $dQ/d\epsilon = E^{-1}[A(\epsilon)\ln E + B(\epsilon)]$, where A and B are functions of ϵ, and the total cross section is given by $Q = E^{-1}[A_T \ln E + B_T]$. The coefficients $A(\epsilon)$ and $B(\epsilon)$ for the particular case of the atomic hydrogen are derived analytically as an expansion with respect to $k=\sqrt{\epsilon}$. The expansion converges for all values of k. By integrating $A(\epsilon)$ and $B(\epsilon)$ with respect to ϵ, A_T and B_T are obtained and compared with the values given by Bethe using a different method. The coefficients of the first two leading terms of the expansion of $dQ/d\epsilon$ with respect to ϵ or $1/\epsilon$ when ϵ is small or large are found. A relationship for the average energy of the ejected electrons is given. Different features of the high-energy impact ionization and a certain connection between the ionization and the discrete level excitation are discussed.

I. FORMULATION

Bethe in a memorable article[1] has shown that for inelastic collision of a charged particle of high energy E with an atom, the cross section depends on E, and linearly on two parameters which are functions of the atomic structure and the energy transferred to the atom. For ionization of an hydrogenic atom of nuclear charge Z by an electron with nonrelativistic high energy E, the cross section per unit range of the energy ϵ of the ejected electron and the total cross section are given, respectively, by

$$dQ/d\epsilon \sim (Z^4 k_1^2)^{-1}[A(\epsilon)\ln k_1^2 + B(\epsilon)]\pi a_0^2, \quad k_1^2 = a_0^2 E/Z^2, \tag{1}$$

$$Q = \int_0^{\epsilon_{\max}} (dQ/d\epsilon)d\epsilon \sim (Z^4 k_1^2)^{-1}[A_T \ln k_1^2 + B_T]\pi a_0^2, \tag{2}$$

with a_0 the Bohr radius and E and ϵ in rydbergs. $A(\epsilon)$ and $B(\epsilon)$ are functions of ϵ. A_T and B_T are dimensionless constants, independent of the nuclear charge, and are integrals of $A(\epsilon)$ and $B(\epsilon)$ with respect to ϵ. $\epsilon_{\max}$ is the maximum value of ϵ. Equations (1) and (2) will be derived here. Bethe has derived (1) and (2), and using sum rules for the generalized oscillator strength he has evaluated A_T and B_T for the hydrogenic atoms. Here $A(\epsilon)$ and $B(\epsilon)$ are derived analytically, and by integrating them over ϵ, values of A_T and B_T are rederived.

With the system of an incident electron and an hydrogenic atom of nuclear charge Z, let $\vec{k}_1'$, $\vec{k}_2'$, and $\vec{k}'$ represent the momenta of the incident, scattered, and ejected electrons, and $\vec{K}' = \vec{k}_1' - \vec{k}_2'$. We take $\hbar = m = 1$ with m the mass of the electron, and throughout we express energy in rydbergs. Then $E = k_1'^2$ and $\epsilon = k'^2$. In this way E and ϵ take the dimension of the inverse of the length squared, but numerically their values are given by rydbergs. Equation for the conservation of energy is given by $k_1'^2 - k_2'^2 = Z^2/a_0^2 + k'^2$ In the Born approximation

$$Q = \int_0^{\epsilon_{\max}} (dQ/d\epsilon)d\epsilon, \tag{3}$$

$$\frac{dQ}{d\epsilon} = \frac{8\pi}{a_0^2 E(Z^2/a_0^2 + \epsilon)} \int_{k_1' - k_2'}^{k_1' + k_2'} \frac{dK'}{K'} \frac{df}{d\epsilon}, \tag{4}$$

where $df/d\epsilon$ is the generalized oscillator strength per unit range of ϵ defined by

$$\frac{df}{d\epsilon} = \frac{Z^2/a_0^2 + \epsilon}{2K'^2} \int k' d\hat{k}' |\langle \vec{k}' | e^{i\vec{K}' \cdot \vec{r}} | 1s \rangle|^2, \tag{5}$$

with $|1s\rangle$ and $|\vec{k}'\rangle$ the ground and the continuum wave functions of the atomic electron. $|k'\rangle$ is normalized such that asymptotically $|\vec{k}'\rangle \sim (2\pi)^{-3/2} \exp i\vec{k}' \cdot \vec{r}$. We introduce the dimensionless vectors $\vec{k}_1$, $\vec{k}_2$, $\vec{k}$, and $\vec{K}$ by $\vec{k}_1' = \mu\vec{k}_1$, $\vec{k}_2' = \mu\vec{k}_2$, $\vec{k}^1 = \mu\vec{k}$, and $\vec{K}' = \mu\vec{K}$, where $\mu = Z/a_0$. Evaluation of $df/d\epsilon$ then leads to [1,2]

$$\frac{dQ}{d\epsilon} = \frac{2^{10}(\pi a_0^2)}{Z^4 E(1 - e^{-2\pi/k})} \int_{k_1 - k_2}^{k_1 + k_2} F(K)dK, \tag{6}$$

$$F(K) = \frac{e^{-2\varphi/k}[K^2 + \frac{1}{3}(1 + k^2)]}{K[1 + 2(K^2 + k^2) + (K^2 - k^2)^2]^3}, \quad \varphi = \tan^{-1}\frac{2k}{K^2 - k^2 + 1} \quad . \tag{7}$$

We seek an expansion of $F(K)$ which would converge for all values of the momentum transfer K. Similar expansion with useful application has been introduced by Lassettre[3] for excitation of the nonhydrogenic atoms and deduction of the form of the differential cross section from experimental data. It is feasible that the present expansion will also find usefulness for ionization of the nonhydrogenic atoms. $F(K)$ in (7) can be expanded in terms of K for small and large values of K, corresponding to the limits of the integral in (6) at high energy, but the integrals of the two expansions may and, in fact, do differ by a constant. To overcome this difficulty we change the variable of integration from K to φ. This results in

$$F(K)dK = -\frac{e^{-2\varphi/k}\sin^4\varphi}{2(2k)^5}\left(1+\frac{\frac{1}{3}(1+k^2)\sin\varphi}{2k\cos\varphi-(1-k^2)\sin\varphi}\right)d\varphi . \tag{8}$$

To separate out the logarithmic term in the integral in (6), we introduce φ_1 as the zeroth-order term of the Taylor's expansion of φ with respect to K^2. Then

$$\varphi_1 = \varphi - \varphi_0, \quad \varphi_0 = \tan^{-1}[2k/(1-k^2)], \tag{9}$$

and by direct substitution

$$\int F(K)dK = \frac{e^{-2\varphi_0/k}}{6(2k)^5(1+k^2)}\int e^{-2\varphi_1/k}\sin^4(\varphi_0+\varphi_1)[2k\cot\varphi_1 - 2(1+2k^2)]\,d\varphi_1. \tag{10}$$

From (7) and (9) it is seen that for all values of K and k, φ_1 lies between 0 and $-\pi$. The transcendental functions in the integrand in (10) can then be expanded in powers of φ_1 and the integration can be carried out term by term. With this procedure we obtain

$$\int F(K)dK = \frac{e^{-2\beta\varphi_0}}{6(1+k^2)}\left(\frac{\ln(\sin\varphi_1)}{(1+k^2)^4} + \frac{1+2k^2}{8(2k)^5}\,\mathrm{Re}(3a^{-1} - 4e^{2i\varphi_0}b^{-1} + e^{4i\varphi_0}c^{-1}) + \frac{1}{(1+k^2)^4}\sum_{m=1}^{\infty}A_m(\varphi_1)\frac{(-2\varphi_1)^m}{m!}\right), \tag{11}$$

$$A_m(\varphi) = \frac{1}{8}\left(\frac{1+k^2}{2k}\right)^4\left[\left(\frac{1}{m} - \sum_{n=1}^{\infty}\frac{2^{2n}B_n\varphi^{2n}}{(m+2n)(2n)!}\right)\mathrm{Re}(3a^m - 4e^{2i\varphi_0}b^m + e^{4i\varphi_0}c^m) + \frac{1+2k^2}{2k}\,\mathrm{Re}(3a^{m-1} - 4e^{2i\varphi_0}b^{m-1} + e^{4i\varphi_0}c^{m-1})\right], \tag{12}$$

where $\beta = 1/k$, $a = \beta$, $b = \beta - i$, $c = \beta - 2i$, and B_n is Bernoulli's number. Re stands for the real part of a complex quantity.

In this way, through (6), $dQ/d\epsilon$ is expressed as a converging sum over φ_1 for any value of the momentum transfer, and the problem of integration is reduced to a summation. For high-energy incident electrons to first order, $k_1 - k_2 = (1+k^2)/2k_1$, and $k_1 + k_2 = 2k_1$. Therefore the lower and the upper limits of the integral in (11) are given at high energy by $\varphi_1 = k/2k_1^2$ and $\varphi_1 = \varphi_0$, respectively. Evaluating (11) at the limits, combining it with (6), and comparing the result with (1) gives

$$A(\epsilon) = 2^9 e^{-2\beta\varphi_0}/3\mu^2(1-e^{-2\pi\beta})(1+k^2)^5, \tag{13}$$

$$B(\epsilon) = A(\epsilon)\left(\sum_{m=1}^{\infty}A_m(\varphi_0)\frac{(2\varphi_0)^m}{m!} - \ln\tfrac{1}{4}(1+k^2)\right). \tag{14}$$

Substitution of (1) into (3) and comparison with (2) shows that

$$A_T = \int_0^\infty A(\epsilon)d\epsilon = \int_0^\infty A(k^2)dk^2, \quad B_T = \int_0^\infty B(\epsilon)d\epsilon = \int_0^\infty B(k^2)dk^2, \tag{15}$$

where, because of the form of $A(\epsilon)$ and $B(\epsilon)$, the upper limits of the integrals have been extended to infinity without loss of accuracy.[4] Here, by definition, $A(k^2) = A(\epsilon)d\epsilon/dk^2 = \mu^2 A(\epsilon)$. Similarly $B(k^2) = \mu^2 B(\epsilon)$, and by (13) and (14) A_T and B_T become independent of the nuclear charge. Numerical evaluation of the integrals in (15) yields

$$A_T = 1.133\,65, \quad B_T = 5.026\,25. \tag{15$'$}$$

This completes the derivation of Eqs. (1) and (2). Using these values of A_T and B_T in Eq. (2) we can write this equation alternatively as

$$Q \sim (4\pi a_0^2 M^2/Z^4 k_1^2)\ln 4Ck_1^2, \quad M^2 = 0.283\,41, \quad C = 1/0.047\,483. \tag{2$'$}$$

Equation (2′) is the form originally given by Bethe with $M^2 = 0.285$ and $C = 1/0.048$. A more accurate evaluation of M^2 and C using Bethe's method has been done by Inokuti,[5] and values given by (2′) are in agreement with these values to all places. Similarly, Inokuti[6] has given the numerical values of $A(\epsilon)$ and $B(\epsilon)$ in slightly different form, and (13) and (14) agree with these results.

II. RESULTS AND DISCUSSION

It is convenient to define by $dQ_0/d\epsilon$ the cross section which is obtained by (4), by replacing the generalized oscillator strength by the optical oscillator strength, $df_0/d\epsilon$, given by the first nonvanishing term of the Taylor's expansion of $\exp i\vec{K}'\cdot\vec{r}$ in (5). Then by straightforward integration,

$$\frac{df_0}{d\epsilon}=\frac{1}{6}\left(\frac{Z}{a_0^{\,2}}+\epsilon\right)\int k'd\hat{k}'\,|\langle\vec{k}'|\vec{r}|1s\rangle|^2=\frac{2^7}{3\mu^2}\frac{e^{-2\pi\beta\varphi_0}}{(1-e^{-2\pi\beta})(1+k^2)^4}\,. \tag{16}$$

Comparison of (16) with (13) shows that

$$A(\epsilon)=\tfrac{2}{3}\mu^2k'\int d\hat{k}'\,|\langle\vec{k}'|\vec{r}|1s\rangle|^2, \tag{17}$$

relating $A(\epsilon)$ to the squared modulus of the dipole moment, integrated over directions of the ejected electron. Substitution of (16) in (4), replacement of the limits in the integral in (4) by their first-order term, and an integration leads with the use of (13) to

$$dQ_0/d\epsilon\sim[2\pi A(\epsilon)/Z^2E]\ln[4k_1^{\,2}/(1+k^2)] \tag{18}$$

Comparison of this with (13) and (14) shows that (1) can be written

$$\frac{dQ}{d\epsilon}\sim\frac{1}{2}\frac{dQ_0}{d\epsilon}+\frac{\pi A(\epsilon)}{Z^2E}\sum_{m=1}^{\infty}A_m(\varphi_0)\frac{(2\varphi_0)^m}{m!} \tag{19}$$

Then the contribution of the small scattering angle, or the equivalently small momentum transfer by the incident electron, to the cross section represented by the logarithmic term in (1) is half the contribution of the dipole term integrated over all range of the momentum transfer. This provides a convenient way to avoid the introduction of a cutoff in the integral in (4) for the distant collisions.

The two terms in (19) correspond to the dipole and the nondipole parts of the cross section, and they are comparable in magnitude throughout the nonrelativistic region of the incident energy (cf. Fig. 3). This is in contrast to the excitation to the low-lying levels of the atoms, where at energies several times the threshold energy the dipole part dominates the total cross section. This also indicates that while photoexcitation is closely related to the high-energy impact excitation, such relationship does not exist between photo-ionization and the electron impact ionization.

An interesting part of the present paper is to find the leading terms of the expansion of $dQ/d\epsilon$ in terms of ϵ or $1/\epsilon$ where ϵ is small or large, respectively. Using the explicit form of $A_m(\varphi)$ given by (12), we find after some algebraic manipulation that we have the following limiting cases when k is small or large:

$$\sum_{m=1}^{\infty}A_m(\varphi_0)\frac{(2\varphi_0)^m}{m!}\sim\mathbf{\Gamma}-2^{-7}(41e^4+11)+2^{-7}(13e^4-\tfrac{443}{3})k^2,\quad k\to0; \tag{20}$$

$$\sim(3\pi k^5/2^6)[1+\pi/k+(1+2\pi^2)/3k^2]\,,\qquad k\to\infty; \tag{21}$$

where $$\mathbf{\Gamma}=\sum_{m=1}^{\infty}\frac{4^m}{m(m!)}=17.6674.$$

It also is necessary to expand $A(\epsilon)$ for small and large ϵ. In doing so we can establish that for $0\leqslant k<1$ the factor $[1-\exp(-2\pi/k)]^{-1}$ which appears in (13) is equal to unity plus terms of the order less than k^{17}. Then for the expansion considered here this factor can be put equal to unity, and we obtain

$$A(\epsilon)\sim(2^9e^{-4}/3\mu^2)(1-\tfrac{11}{3}k^2),\qquad k\to0; \tag{22}$$

$$A(\epsilon)\sim(2^8/3\mu^2k^9)[1-\pi/k+(\pi^2-3)/3k^2],\quad k\to\infty. \tag{23}$$

Substitution of (20) through (23) into (14) leads to

$$B(\epsilon)\sim\frac{1}{\mu^2}(B_0-B_1k^2),\ k\to0;\quad B_0=4.62393,\quad B_1=6.35310; \tag{24}$$

$$B(\epsilon)\sim(4/\mu^2k^4)(1-2/3k^2),\qquad k\to\infty\,. \tag{25}$$

With these values of $A(\epsilon)$ and $B(\epsilon)$, Eq. (1) can be written

$$dQ/d\epsilon \sim (Z^6 k_1^2)^{-1}[(A_0 - A_1 k^2)\ln k_1^2 + B_0 - B_1 k^2]\,\pi a_0^4, \quad E \gg 1 \gg \epsilon;$$

$$k^2 = a_0^2\epsilon/Z^2, \quad A_0 = 3.125\,87, \quad A_1 = 11.4615; \tag{26}$$

$$dQ/d\epsilon \sim [4\pi a_0^2/E(a_0^2\epsilon)^2](1 - 2Z^2/3a_0^2\epsilon), \quad 1 \ll \epsilon \ll E. \tag{27}$$

Equation (26) is a valid expression when the incident and the scattered electrons have high energies, and the secondary electron has low energy. Most contribution to the total cross section is due to this energy region of the secondary electron. Equation (26) is related to the excitation to a high principal quantum number n of the normal state of the hydrogen atom in the following way.[7] Let $Q(n)$ be the excitation cross section. By writing $\epsilon = -Z^2 n^{-2} a_0^{-2}$, where ϵ is the energy of the states with the principal quantum number n, and noticing that $dQ/d\epsilon$ is a continuous function of ϵ when ϵ becomes negative, through the relationship $Q(n)dn = (dQ/d\epsilon)d\epsilon$ we obtain, up to n^{-4} terms

$$Q(n) \sim 2(n^3 Z^4 k_1^2)^{-1}[(A_0 + A_1/n^2)\ln k_1^2 + (B_0 + B_1/n^2)]\,\pi a_0^2, \quad n \gg 1. \tag{28}$$

Brown[8] has evaluated $Q(n)$ for $n \gg 1$ by an independent method, and (28) agrees with his results. Similarly, for high n and high incident energies, (28) is in agreement with the results of the numerical integration of $Q(n)$ by the author.[9]

Concerning Eq. (27) the leading term in this equation is the same as the elastic cross section between two electrons in a frame of reference where one of the electrons is initially at rest and its energy becomes ϵ after the collision. The cross section in this case is the same classically and quantum mechanically, the classical cross section being given by the Rutherford formula,[10] and the quantum-mechanical one by the Moeller's formula.[11] The reason for the agreement of the leading term with the elastic cross section is given in Ref. 10. Equation (27) in addition gives a second-order term which is due to the binding of the atomic electron to the nucleus. This term agrees with the classical calculation where quantum-mechanical momentum distribution is assumed for the bound electron.[11a]

When ϵ becomes comparable to E, the next higher term in E and also the contribution from the second Born approximation should be included in (27). In addition, the exchange effect for the identity of the two electrons should be taken into account. Because of the difficulty in calculating the second Born approximation, this will not be done here. Neglecting the second term in (27), the inclusion of the exchange effect in the leading term of (27) leads to the Mott's formula[10]

$$dQ/d\epsilon \sim (4\pi/a_0^2 E)[1/\epsilon^2 + 1/(E-\epsilon)^2 - 1/\epsilon(E-\epsilon)], \quad \epsilon, E \gg 1. \tag{29}$$

Concerning the contribution of the exchange effect to the total cross section, it should be pointed out that this is of the order of $1/E$, and therefore it becomes negligibly small at high enough incident energies. This can be seen by integrating (27) over the energy region where ϵ is comparable to E.

A quantity of interest is the average energy of the ejected electrons in an ionization process. This quantity will be calculated below. By definition

$$\bar{\epsilon} = \int_0^{\epsilon_{\max}} \epsilon\,(dQ/d\epsilon)d\epsilon \Big/ \int_0^{\epsilon_{\max}} (dQ/d\epsilon)d\epsilon\,. \tag{30}$$

By writing $\epsilon = \mu^2 k^2$ and by making use of (1), we find that

$$\bar{\epsilon} \sim (Z/a_0)^2\left\{\int_0^{k_1^2-1}[A(k^2)\ln k_1^2 + B(k^2)]dk^2\right\}^{-1}\left\{\int_0^{k_1^2-1} k^2[A(k^2)\ln k_1^2 + B(k^2)]dk^2\right\}. \tag{31}$$

The integrals occurring in the denominator of (31) are given by (2). When k is large, $A(k^2)$ and $B(k^2)$ are proportional to k^{-9} and k^{-4}, respectively [cf. Eqs. (23) and (25)]. The upper limit of the integral with respect to $A(k^2)$ in the numerator of (31) can then be put equal to infinity. For the integral with respect to $B(k^2)$, we have up to the first-order terms

$$\int_0^{k_1^2-1} k^2 B(k^2)dk^2 = \int_0^a k^2 B(k^2)dk^2 + \int_a^{k_1^2-1}(4/k^4)k^2 dk^2 = \int_0^a k^2 B(k^2)dk^2 - 4\ln a + 4\ln(k_1^2 - 1), \tag{32}$$

where a is a value of k^2 at which $B(k^2)$ reaches its asymptotic form. In this way we find that

$$\bar{\epsilon} = (Z/a_0)^2(C\ln k_1^2 + D)/(A_T\ln k_1^2 + B_T), \tag{33}$$

with C and D dimensionless constants given by

$$C = 4 + \int_0^\infty k^2 A(k^2)dk^2 = 4.606, \quad D = \int_0^a k^2 B(k^2)dk^2 - 4\ln a = -2.123, \tag{34}$$

and A_T and B_T given by (15′).

It is more appropriate to use an asymptotic form for $B(k^2)$ in which the exchange effect is taken into account. Comparison of the leading term of (25) with (29) shows that when exchange is included the asymptotic form of $B(k^2)$ is given by $4\{k^{-4}+(k_1{}^2-k^2)^{-2}-[k^2(k_1{}^2-k^2)]^{-1}\}$. By making use of this form in (31), and noticing that when exchange is included $\epsilon_{\max}=\frac{1}{2}\mu^2(k_1{}^2-1)$, we find that (33) is still valid provided we replace D in this equation by

$$D^{\mathrm{ex}}=D+4(1-\ln 8)=-6.441. \tag{35}$$

It should be realized that although both the numerator and the denominator of (33) are of the form $\ln k_1{}^2$ + constant, the origin of the logarithmic terms is quite different. The term in the denominator comes entirely from small momentum-transfer collisions; that in the numerator, partly from these and partly from large momentum-transfer collisions. This indicates a large spread in the energy of the ejected electrons.

With or without exchange, $\bar{\epsilon}$, as the incident energy increases, reaches a limit given by $(C/A_T)(Z/a_0)^2 = 4.063\ Z^2$ Ry. Then the maximum value of $\bar{\epsilon}$ for an electron bounded to a central charge Z is proportional to its binding energy, although from (33) it is seen that the higher Z, the higher the incident energy at which this maximum is reached. For many-electron atoms it can be said that the maximum value of the average energy of an ejected electron is roughly proportional to the square of the effective charge seen by the electron before its ejection.

We also notice that for atomic hydrogen the maximum energy loss by the incident electron cannot exceed 5.063 Ry. Bethe[1,10] has shown that the energy loss by an electron in an inelastic collision with the hydrogen atom reaches the value of 2 Ry at high energy, and that 28.34% of the collisions lead to ionization. Using this information we find that at high incident energies the average energy loss of an incident electron in excitation of all the discrete states of the atomic hydrogen reaches the value of 0.7887 Ry.

Figures 1 through 4 illustrate some of the results obtained. Figure 1 is the well-known graphical comparison of the Bethe approximation with the Born approximation, given here for the specific case of ionization. Z^2EQ is plotted versus $\ln(E/Z^2)$, where by Eq. (2) a straight line is obtained for the Bethe approximation. In the case of the atomic hydrogen, the two approximations agree with each other for energies larger than about 20 threshold units. For atoms with larger central charge, the agreement is reached at still higher energies.

Figure 2 is a plot of the dimensionless coefficients $A(k^2)$ and $B(k^2)$ versus the dimensionless parameter $k^2=a_0{}^2\epsilon/Z^2$. The coefficient $A(k^2)$ which is proportional to the dipole moment, Eq. (17), is appreciable only for small values of k^2, corresponding to the small momentum transfer by the incident electron arising from the distant collisions. For large k^2 it falls off as k^{-9}. The coefficient $B(k^2)$ approaches its classical limit of $4/k^4$ given by the Rutherford formula. The figure shows clearly the transition between the quantum region, small ϵ, and the classical region, large ϵ. In the classical impulse approximation[12-16] the total ionization cross section at high incident energy is specified by (2) where $A_T=0$ and $B_T=\frac{20}{3}$.

In Fig. 3 the ratio of the logarithmic part of the cross section as given by (2) to the total cross section is plotted. It is evident that contribution of the dipole term given by the logarithmic term to the total cross section remains a fraction of the total cross section for the whole nonrelativistic range of the incident energies.

In Fig. 4 a plot of the average energy of the ejected electrons versus the incident energies is given. The average energy reaches the limit of $4.063Z^2$ Ry as the incident energy tends to infinity, signifying the limit of the impulse received by the atom. Relativistic corrections are neglected.

To complete the discussion, we list the coefficients $A(n)$ and $B(n)$ originally given by Bethe for the elec-

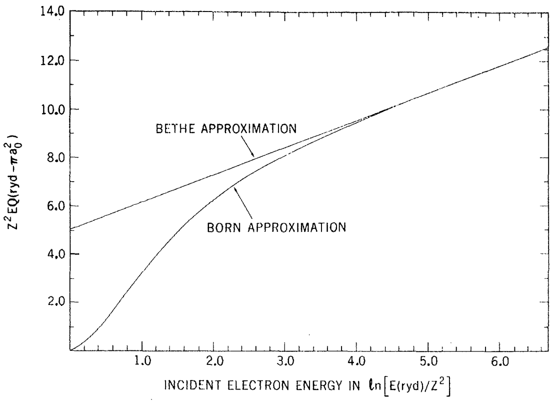

FIG. 1. A comparison of the Bethe's approximation, Eq. (2), with the Born approximation. Q is the ground-state ionization of an hydrogenic atom.

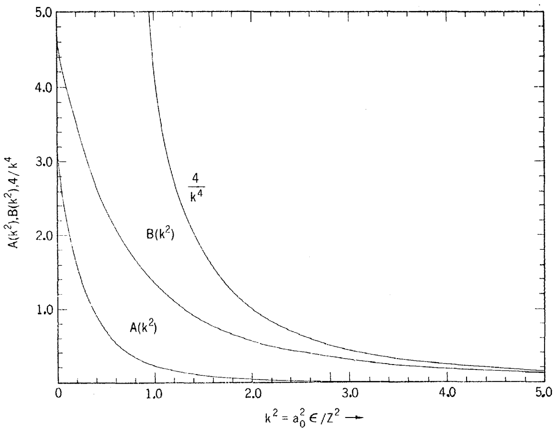

FIG. 2. A plot of the coefficients $A(k^2)$, $B(k^2)$, and $4/k^4$.

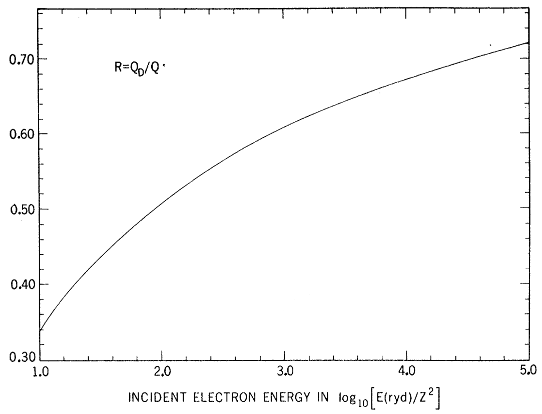

FIG. 3. Q_D is the logarithmic part of Eq. (2) and R is the ratio of this part to the total cross section.

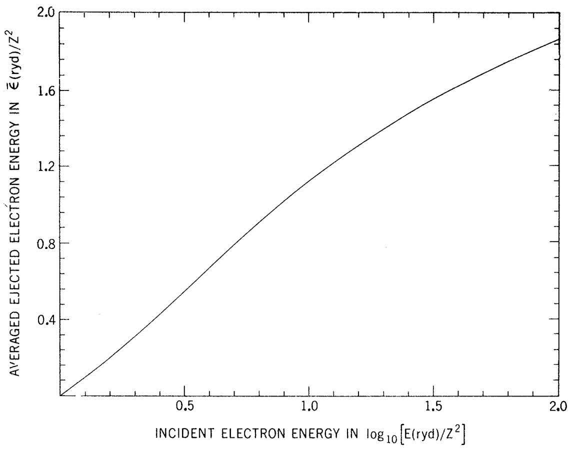

FIG. 4. A plot of the average energy of the ejected electron versus the incident energy. The Born approximation has been used for incident energies less than 25 Ry, and Eq. (33) for energies above this value.

TABLE I. Values of $A(n)$ and $B(n)$.

n	2	3	4	5	6	7	8	9	10	11	12
$n^3A(n)$	17.7577	9.6108	7.9165	7.2596	6.9313	6.7423	6.6231	6.5430	6.4863	6.4448	6.4135
$n^3B(n)$	12.2396	10.7054	10.0612	9.7647	9.6051	9.5096	9.4478	9.4056	9.3755	9.3533	9.3364

tron impact excitation. Recalling the definition of $Q(n)$ we can write, in analogy to (1),

$$Q(n)=(Z^4k_1^{\,2})^{-1}[A(n)\ln k_1^{\,2}+B(n)]\pi a_0^{\,2},\quad k_1^{\,2}=a_0^{\,2}E/Z^2. \tag{36}$$

The dimensionless constant and charge-independent coefficients $A(n)$ and $B(n)$ are given for $n=2$ through $n=12$ in Table I.[17] For higher values of n, Eq. (28) can be used.

It is interesting to notice that the ratio A/B for excitation and ionization is a monotonically decreasing function of the energy transferred to the atom, and at high energy transfer it approaches zero. The ratio of the logarithmic term to the nonlogarithmic term in the cross section is $(A/B)\ln k_1^{\,2}$. For an incident energy of 1000 Ry and $Z=1$, this ratio is 10.022 for $n=2$ excitation, and is 1.558 for ionization.

The foregoing results for electron impact ionization and excitation are also applicable to the proton impact ionization and excitation. This results from the fact that the cross section is proportional to the square of the charge of the projectile, and in the approximation stated following Eq. (12), it depends on the initial relative velocity of the projectile-target atom only, and is independent of the reduced mass of the system (cf. Ref. 2). Thus all equations derived so far can be used for proton impact, provided E is replaced by $(m/M)E_p$, where M and E_p are the mass and energy of the incident proton. In this way (36) agrees with the high-energy analytical expression of Bates and Griffing[18] up to, and excluding, the k_1^{-4} terms for $n=2$ and $n=3$ proton impact excitation; and (2) gives the same value at 3.5 MeV incident protons as the graphical Born calculation of Bates *et al.*[18], and Peach,[19] for proton impact ionization.

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[1] H. A. Bethe, Ann. Phys. (Lpz.) 5, 325 (1930).

[2] N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford University Press, London, 1965), 3rd ed., p. 489.

[3] E. N. Lassettre, J. Chem. Phys. 43, 4479 (1965).

[4] For $\epsilon \gg 1$ it is seen from (23) and (25) that $A(\epsilon)\ \alpha\ \epsilon^{-9/2}$ and $B(\epsilon)\ \alpha\ \epsilon^{-2}$.

[5] M. Inokuti, Argonne National Laboratory Report No.

ANL-6769, 1963 (unpublished).

[6] M. Inokuti, Argonne National Laboratory Report No. ANL-7220, 1966 (unpublished).

[7] R. McCarroll, Proc. Phys. Soc. (London) A70, 460 (1957).

[8] L. M. Brown, Phys. Rev. 79, 297 (1950).

[9] K. Omidvar, Phys. Rev. 140, A38 (1965). See also Ref. 7.

[10] L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), Chap. 15.

[11] Ref. 2, p. 818.

[11a] J. D. Garcia, Phys. Rev. 177, 223 (1969). L. Vriens and M. Inokuti, private communication.

[12] M. Gryzinski, Phys. Rev. 115, 374 (1958).

[13] R. C. Stabler, Phys. Rev. 133, A1268 (1964).

[14] L. Vriens, Proc. Phys. Soc. (London) 89, 13 (1966).

[15] J. D. Garcia, Phys. Rev. 159, 39 (1967).

[16] R. Abrines, I. C. Percival, and N. A. Valentine, Proc. Phys. Soc. (London) 89, 515 (1966), give a statistical solution of the exact classical problem, but B_T is not specified in their work.

[17] These numbers with slightly different forms are given by Inokuti in Ref. 5, and they have been independently calculated and checked by the author.

[18] D. R. Bates and G. Griffing, Proc. Phys. Soc. (London) A66, 961 (1953). See also R. M. May, Phys. Letters 14, 98 (1965).

[19] G. Peach, Proc. Phys. Soc. (London) 85, 709 (1965).

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Vibrational Excitation in Ion-Molecule Collisions: H^+, $H_2{}^+$, He^+, N^+, Ne^+, and Electrons on N_2 †

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A study has been made of the relative band intensities of the $\Delta v = -1$ sequence of the $N_2{}^+$ first negative system excited by H^+, $H_2{}^+$, He^+, N^+, Ne^+, and electrons. Projectile ion laboratory velocities from 6×10^6 to 1.7×10^8 cm/sec (100 eV to 13.5 keV) were used. At ion velocities greater than 10^8 cm/sec, the relative band intensities were found to agree with those predicted by the Franck-Condon principle and found in excitation by 150-eV electrons. Below this velocity the relative population of higher ($v' > 0$) vibrational states increased monotonically. At the lowest velocity used, the populations of the $v' = 0$ and $v' = 1$ vibrational states of $N_2{}^+$ $B\,{}^2\Sigma_u{}^+$ were found to be equal within experimental error while the higher-state populations increased many orders of magnitude above those predicted by the Franck-Condon principle. The vibrational excitation was found to be solely dependent on the projectile ion's laboratory velocity and independent of its chemical identity. No vibrational excitation was observed in the N_2 second positive system excited under similar conditions. It is suggested that the excitation effects in the $N_2{}^+$ first negative system occur by a mechanism involving perturbation of the target molecule's vibrational wave functions by the projectile ion. Implications of these results for other collision studies as well as atmospheric phenomena are discussed.

INTRODUCTION

Experimental studies of vibrational excitation in ion-molecule collisions are of considerable importance since theory does not provide an adequate basis for the prediction of the vibrational energy distribution in the products of such interactions. The Franck-Condon principle, which is of great use in describing a wide variety of excitation and spectroscopic phenomena, is difficult to apply in the case of certain slow ion-molecule collisions where the molecular vibrational wave functions may be significantly distorted. This paper presents data we have obtained from experiments in which the products of collisions between a variety of atomic and molecular ions and N_2 have been studied spectroscopically to measure the vibrational energy distribution of the target after excitation.

It is known that in the case of electron excitation, the vibrational energy distribution of excited electronic states can certainly be well described by the Franck-Condon principle if the electron energy is greater than 100 eV.[1] In such a case, if the process involves excitation of a molecule which is initially in the ground electronic and vibrational states, $X(v''=0)$, to some excited electronic and vibrational state, $B(v'=i)$, the ratio of the population of the ith vibrational state of B to the population of the ground vibrational state of B is given by the ratio of the Franck-Condon factors for the two transitions $X(v''=0) \rightarrow B(v'=0)$ and $X(v''=0) \rightarrow B(v'=i)$:

$$N_i/N_0 = q_i{}^{X\rightarrow B}/q_0{}^{X\rightarrow B}. \tag{1}$$