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Theory of the Scattering of Slow Electrons by Diatomic Molecules

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The problem of the Ramsauer effect for diatomic molecules has been treated in a manner analogous to that used by Allis and Morse for atoms. The molecule is represented by a simplified potential field in spheroidal coordinates, and an exact solution is obtained, valid for all velocities of incident electrons. The calculations of "total cross section for elastic scattering" are made in terms of three parameters whose values for a given molecule are definitely determined from data of band spectroscopy and from Slater's rules for atomic shielding constants. Calculations have been carried out in the region of incident electron velocities 0 to 40 volts for N_2, O_2, and H_2, for which molecules excellent agreement is obtained with experiment.

1. Introduction

Measurements of the absorption of slow electrons in their passage through a gas have revealed that for molecules, as well as for atoms, the absorption coefficient, α, may change by large amounts for small changes in the velocity of the incident beam, in the range of electron velocities from 0 to 10 or 15 electron volts. The measurements of α, referred to 0°C and 1 mm of mercury pressure, may be correlated with the total cross section for scattering, Q, by the expression $Q=1.02\alpha$ where Q is measured in terms of the square of the first Bohr orbit of hydrogen.

The success of the quantum theory in the hands of Allis and Morse,[1] in resolving this Ramsauer effect for atoms, by assuming a simplified potential, suggested naturally that the molecular problem might be treated in an analogous way. The results of Allis and Morse indicate that the collision cross section is not sensitive to charge distribution provided the potential has the proper characteristics. Their potential was Coulomb-like at small values of r, but went to zero at some distance r_0 from the nucleus. This assumes that the negative charge is distributed over a spherical shell of radius r_0. The effective charge number, and the value of r_0 were calculated from the empirical rules of Slater[2] for the various atoms.

Presumably the molecule may be represented in a similar fashion. Experimental data are available for the internuclear distances, while the other molecular constants, effective charge numbers, and the equivalent of r_0, cannot come far wrong if the atomic analogy be adopted *in toto*.

2. The Molecular Field

Mathematical treatment of the scattering from diatomic molecules requires the wave equation in spheroidal coordinates. Fig. 1 indicates this orthogonal coordinate system where d is the internuclear distance, r_1 and r_2 are the distances from the two nuclei, and

$$\xi=(r_1+r_2)/d\,;\quad \eta=(r_1-r_2)/d.$$

For a symmetrical diatomic molecule the Coulomb potential is given by

$$\Phi_c=2Z\left(\frac{1}{r_1}+\frac{1}{r_2}\right)=\frac{8Z}{d}\cdot\frac{\xi}{\xi^2-\eta^2}\tag{1}$$

(in atomic units). In order that the potential, Φ, shall represent the field of a molecule it must go to zero on some boundary, such as $\xi=\xi_0$ $=$constant. But, at the same time, it must leave the Schrödinger equation separable. In other words, Φ must be equal to the Coulomb potential Φ_c multiplied by some function $f(\xi)$, such that

$$\begin{aligned}\Phi &\simeq \text{Coulomb} &&\text{for}\quad \xi\simeq 1\\ &=0 &&\text{for}\quad \xi=\xi_0.\end{aligned}$$

The criteria for the function, $f(\xi)$, are

$$\begin{aligned}f(1)&=1, & f'(\xi_0)&\leqq 0,\\ f(\xi_0)&=0, & f'(1)&\leqq 0.\end{aligned}\tag{2}$$

There are numerous forms of $f(\xi)$ which fulfill

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[1] Allis and Morse, Zeits. f. Physik **70**, 567 (1931).

[2] Slater, Phys. Rev. **36**, 57 (1930).

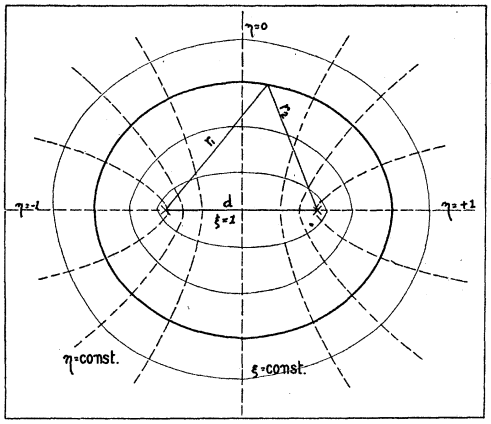

FIG. 1. Spheroidal coordinate system. The heavy line is for $\xi=2$.

these conditions. In order to choose among them it is necessary to examine the charge distribution corresponding to each form, and to select that one which best represents the molecule, and which is at the same time simple enough to make the calculations possible.

The following forms of $f(\xi)$ are typical of a number which have been studied:

$$f_A(\xi)=1-[\xi_0/(\xi_0-1)^2][(\xi-1)^2/\xi],$$

$$f_F(\xi)=(\xi_0-\xi)/(\xi_0-1),$$

$$f_S(\xi)=[(\xi_0-\xi)/(\xi_0-1)]^2.$$

These functions, which multiply Φ_C to give Φ, satisfy all the conditions (2). Other f's involving ξ in higher powers may be written down readily. While these latter may possibly represent the charge distribution in a molecule more accurately, it must be kept in mind that the practical problem of solving the wave equation presents itself.

Forms A and F involve ξ, while form S involves ξ^2. Hence, if A or F give reasonable charge distributions they will be preferred. The charge distribution may be readily calculated from Poisson's equation. ρ_A is given by

$$\rho_A=\frac{2\xi_0 Z}{\pi d(\xi_0-1)^2}\cdot\frac{1-\cos^2(\mathbf{r}_1\mathbf{r}_2)}{r_1 r_2}.$$

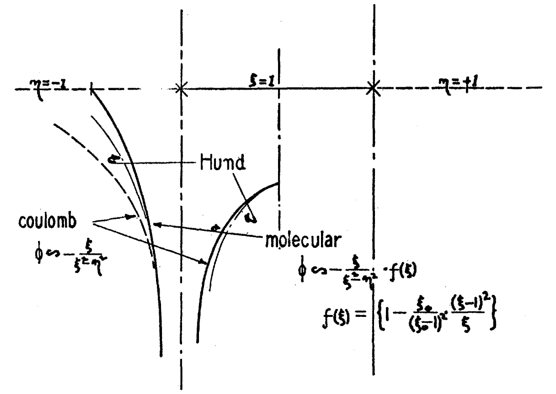

FIG. 2. Potentials plotted along the line of centers of the nuclei.

Φ_A, therefore, represents a distribution of positive charge within the molecule, most of it being concentrated at the two nuclei, none along the line of centers. Or, otherwise, the positive nuclear charge may be considered as being spread out slightly; the negative charge being distributed over the spheroidal surface.

Similarly, ρ_F and ρ_S may be calculated. Φ_F represents both positive and negative charge within the molecule, with a large dipole at each nucleus. Φ_S, which was used by Stier[3] in a calculation for N_2, also has this unsatisfactory dipole at the two centers. The several Φ's do not look appreciably different when plotted together. Φ_A, on a section through the line of centers of the two nuclei, is shown in Fig. 2. The light line is that calculated by Hund using Thomas-Fermi ideas.

Φ_A appears to be best suited to the problem. It avoids the dipoles at the nuclei; it contains ξ in only the second power; and it resembles the Coulomb field as is desired. The additional charge within the molecule may be calculated by integrating over the spheroid, giving for the ρ_A chosen:

$$\int \rho_A d\tau=\frac{2Z}{d}\left[\frac{(\xi_0+1)^2}{2\xi_0}\ln\frac{\xi_0+1}{\xi_0-1}-1\right]=F_0.$$

ξ_0	1.5	2.0	2.5	3.0	4.0
F_0	2.23	1.48	1.07	0.85	0.60

Having chosen a value of ξ_0, F_0 then gives a factor by which the atomic number must be corrected.

It would be desirable, of course, to have a potential which distributed negative charge

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[3] Stier, Zeits. f. Physik **76**, 439 (1932).

throughout the molecule to avoid the necessity of having the negative spheroidal surface charge; the positive charge being only at the two nuclei. This appears to be impossible if, at the same time, one demands that the wave equation be solved analytically. The results of Allis and Morse give justification for the use of the molecular potential which has been selected.

3. Calculation of the Total Cross Section for Elastic Scattering

Using the potential field, Φ_S, previously described, Stier[3] has worked through the problem in spheroidal coordinates for N_2, subject to the condition that the energy of the incoming electron be small. Choosing arbitrarily a value of Z, the effective charge, and ξ_0, the shape of the molecule, he has obtained fair agreement with experiment.

The method to be developed presently will be valid for all velocities of incident electrons, and for all symmetrical diatomic molecules. Its chief restriction lies in the potential function, which is subject to the conditions previously enumerated. This difficulty is inherent in all scattering problems.

It is necessary now to obtain two solutions of the wave equation: one outside, and one inside the molecule. One can then determine the amount of "phase" which must be added to the wave outside of the molecule to have it fit onto the inside wave at $\xi=\xi_0=$molecular boundary.

The solution outside the molecule, $(V=0)$, can be given in terms of the spheroidal functions, recently defined by Stratton,[4] to be

$$\Psi_0=\sum_{m,\,l} A_{ml}e^{im\varphi}(1-\eta^2)^{m/2}(\xi^2-1)^{m/2} \times Se^{(1)}_{m,\,l}(c,\,\eta)\cdot Re^{(1)\text{ or }(2)}_{m,\,l}(c,\,\xi), \quad (3)$$

where the $Se^{(1)}_{m,\,l}(c,\,\eta)$ are expressed as an infinite series of Legendre polynomials;

$$Re^{(1)}_{m,\,l}(c,\,\xi)=\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\frac{(c\xi)^{-m-\frac{1}{2}}}{2^m m!}\sum_k{}' i^{m-k}\frac{(2m+k)!}{k!} \times d_k^{ml}J_{k+m+\frac{1}{2}}(c,\,\xi) \quad (4)$$

and $Re^{(2)}_{m,\,l}(c,\,\xi)$ is a similar expression involving the Neumann function in place of the Bessel function.

The solution inside the molecule,

$$V=(d/2)^2[\xi/\xi^2-\eta^2]f(\xi),$$

differs from (3) only in the ξ part. After separation of variables, the ξ part of the wave equation becomes

$$\left[\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi}-\frac{m^2}{\xi^2-1}+c^2\xi^2 +2Zd\left\{\xi-(\xi-1)^2\frac{\xi_0}{(\xi_0-1)^2}\right\}-\gamma\right]X=0, \quad (5)$$

the solution of which is

$$X(\xi)=(\xi^2-1)^{m/2}\cdot e^{-\lambda(\xi-1)}\cdot f(\xi-1), \quad (6)$$

where $\lambda^2=\alpha-c^2$; $\alpha=2Zd\xi_0/(\xi_0-1)^2$;

$$c^2=(\pi d/\lambda)^2=((d/2)\cdot k)^2.$$

The equation for $f(\xi-1)$ is solved by an infinite series giving a three-term recursion relationship. This series is absolutely convergent for $\xi<3$.

In terms of these two solutions and their first derivatives one proceeds then to obtain the "phase-defects." Equating the ratio of slope to function at the boundary $\xi=\xi_0$ for the solution inside and the solutions outside the molecule

$$\frac{C_{ml}Re^{(1)'}_{m,\,l}(c,\,\xi_0)+D_{ml}Re^{(2)'}_{m,\,l}(c,\,\xi_0)}{C_{ml}Re^{(1)}_{m,\,l}(c,\,\xi_0)+D_{ml}Re^{(2)}_{m,\,l}(c,\,\xi_0)}=g_{ml}=\frac{f'(\xi_0)}{f(\xi_0)}-\lambda, \quad (7)$$

one obtains for the tangent of the "phase-defect"

$$\tan\delta_{ml}=(-1)^m\frac{D_{ml}}{C_{ml}}=(-1)^m\left[\frac{Re^{(1)'}_{m,\,l}(c,\,\xi_0)-g_{ml}\cdot Re^{(1)}_{m,\,l}(c,\,\xi_0)}{g_{ml}Re^{(2)}_{m,\,l}(c,\,\xi_0)-Re^{(2)'}_{m,\,l}(c,\,\xi_0)}\right]. \quad (8)$$

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[4] Stratton, Proc. Nat. Acad. Sci. **21**, 51 (1935).

One wishes then to know the total cross section for elastic scattering in terms of the phase defect. If, from the wave function (3), the expression for a plane wave be subtracted, the scattered wave will be obtained, valid in the range of observation. Morse[5] has recently given the expansion of a plane wave in spheroidal coordinates to be

$$e^{ikX}=2\sum_{m,\,l}\cos\left[m(\varphi-\alpha)\right]\frac{c^m i^{m+l}}{N_{ml}}\sin^m\omega\cdot Se^{(1)}_{m,\,l}(c,\cos\omega)(\sinh\mu\sin\vartheta)^m Se^{(1)}_{m,\,l}(c,\cos\vartheta)Re^{(1)}_{m,\,l}(c,\cosh\mu),\quad(9)$$

where N_{ml} is a normalizing factor;

$$\sinh\mu=(\xi^2-1)^{\frac{1}{2}};\quad \sin\vartheta=(1-\eta^2)^{\frac{1}{2}};\quad X=(d/2)\left[\cos\omega\cos\vartheta\cosh\mu+\sin\omega\sinh\mu\cos(\varphi-\alpha)\right];$$

and the direction of propagation with respect to the z axis is defined by the angles ω and α.

Subtracting e^{ikX} from Ψ one obtains for the scattered wave $F(\vartheta)\cdot e^{ic\xi}/\xi\cdot d/2$, where

$$F(\vartheta)=2\sum_{m,\,l}\frac{\cos\left[m(\varphi-\alpha)\right]}{k\cdot N_{ml}}\cdot(\sin\vartheta\sin\omega)^m\cdot Se^{(1)}_{m,\,l}(c,\cos\vartheta)Se^{(1)}_{m,\,l}(c,\cos\omega)\sin\delta_{ml}e^{i\delta_{ml}},\qquad(10)$$

the A_{ml} of (3) having been so chosen that the solution (10) represents only an outgoing wave.

Averaging $F(\vartheta)$ over all orientations of the molecular axis one obtains the scattered intensity

$$|F(\vartheta)|^2=I(\vartheta)=\frac{4\pi}{k^2}\sum_{m,\,l}\frac{1+\delta_{0m}}{N_{ml}}\sin^{2m}\vartheta\left[Se^{(1)}_{m,\,l}(c,\cos\vartheta)\right]^2\sin^2\delta_{ml},\qquad(11)$$

where δ_{0m} is the Kronecker δ-symbol. The total cross section, Q, is obtained immediately from (11) by integrating over ϑ, giving

$$Q=\frac{4\pi}{k^2}\sum_{m,\,l}(2-\delta_{0m})\sin^2\delta_{ml}=4\pi\left(\frac{d}{2}\right)^2\sum_{m,\,l}q_{ml}.\qquad(12)$$

The q_{ml} are known as "partial cross sections." The contribution of each to the total cross section, Q, arises from different values of m and l; that is, from different angular momenta of the incoming electrons about the molecule.

Q is calculated in terms of three parameters whose values are fixed for a given molecule by Slater's[2] empirical rules for atomic shielding constants, and by data of band spectroscopy. These parameters are:

$$\beta^2=(Z^*\cdot d\cdot\xi_0)/4;\quad x=\xi_0\cdot c;\quad\text{and}\quad\xi_0.$$

The parameter ξ_0 was chosen to be equal to 2 since this assumes, effectively, that the internuclear distance, d, is twice the "atomic radius," and that the formation of a molecule from two atoms does not push negative charge far beyond the atomic radius on a continuation of the line of centers. The shape of the molecule for $\xi_0=2$ is shown in Fig. 1 by the heavy line. A series of calculations for different values of ξ_0 showed that the cross section was quite insensitive to variations in ξ_0 for ξ_0 between 1.75 and 3.0. This choice of $\xi_0=2$ makes the other parameters

$$\alpha=8\beta^2;\quad c^2=x^2/4;\quad\text{and}\quad\lambda=(8\beta^2-x^2/4)^{\frac{1}{2}}.$$

A ξ_0 having been chosen, β then determines the molecule uniquely, since Z^* may be calculated. x is the energy of the incident electron in units proportional to (electron volts)$^{\frac{1}{2}}$. β and x have been defined in this manner since they reduce in the limit to the parameters used by Allis and Morse. A series of calculations varying β and x independently should show any periodic phenomena.

The low velocity limit of $Q(x\rightarrow0)$ may be obtained by use of Eq. (4). For example: when $m=0$, $l=0$

$$\frac{C}{D}=\underset{\xi\rightarrow0}{\tan\delta_{00}}=\frac{g_{00}}{g_{00}+1/\xi_0}\cdot\frac{J_{\frac{1}{2}}(c\xi_0)}{J_{-\frac{1}{2}}(c\xi_0)}\rightarrow0,$$

but
$$\underset{x\rightarrow0}{q_{00}}=2\cdot\frac{\sin^2\delta_{00}}{c^2}\backsimeq2\xi_0{}^2\left[\frac{\xi_0\cdot g_{00}}{\xi_0\cdot g_{00}+1}\right],$$

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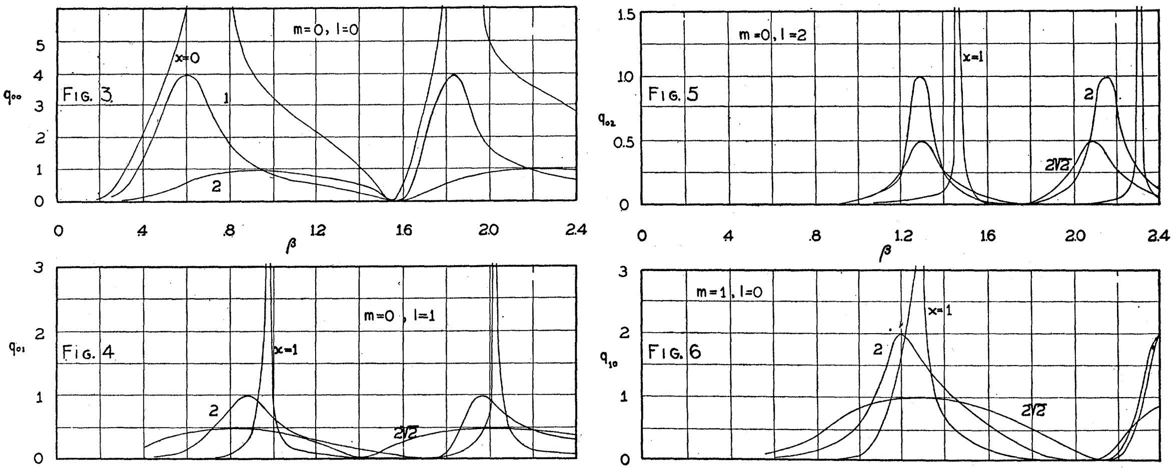
[5] Morse, Proc. Nat. Acad. Sci. **21**, 56 (1935).



FIGS. 3, 4, 5, 6. Partial cross section as function of the parameter β for different electron velocities, showing occurrence of peaks, and periodicity.

giving a finite value of Q as the energy of the incident electron approaches zero. When $m \neq 0$, $l \neq 0$, the q_{ml} approach zero rapidly as $x \to 0$.

5. RESULTS OF CALCULATIONS

The total cross section for elastic scattering, Q, has been calculated as a sum of the partial cross sections q_{ml}. The q_{ml} have been calculated as functions of β for a number of values of m and l and for velocities of incident electrons ranging from 0 to 40 volts. It is observed that strong maxima occur in q_{ml} for small values of x as β increases, and that q_{ml} is periodic in β. Figs. 3 through 6 show this behavior for $m=0, 1$; $l=0, 1, 2$ for several values of x. It is observed that as l increases for a given m, the value of β at which a maximum occurs increases. Similarly, for a given l the first peak of q_{ml} for $m>0$ occurs at a considerably larger value of β than for $m=0$. Hence, for small β, the q_{ml} are not affected by neglect of contributions for values of m and l beyond those given.

It is instructive to plot the phase defects, δ_{ml}, for various velocities as functions of β. This has been done for two different m and l combinations in Figs. 7 and 8. The plot brings out the periodicity again indicating the same sort of correlation with the periodic table as was evident in the atomic problem. Here useful information may be obtained concerning the maxima and minima by considering $\sin \delta_{ml}/c$.

Having obtained the q_{ml} as functions of β for various velocities, and for all values of m and l for which there is any appreciable contribution, one can then plot the total cross section Q, as a function of the velocity of incident electrons, for any β. It is to be noted that neglect of partial cross sections beyond q_{00} and q_{01} may lead to serious error. Each q_{ml} becomes most important for some value of β.

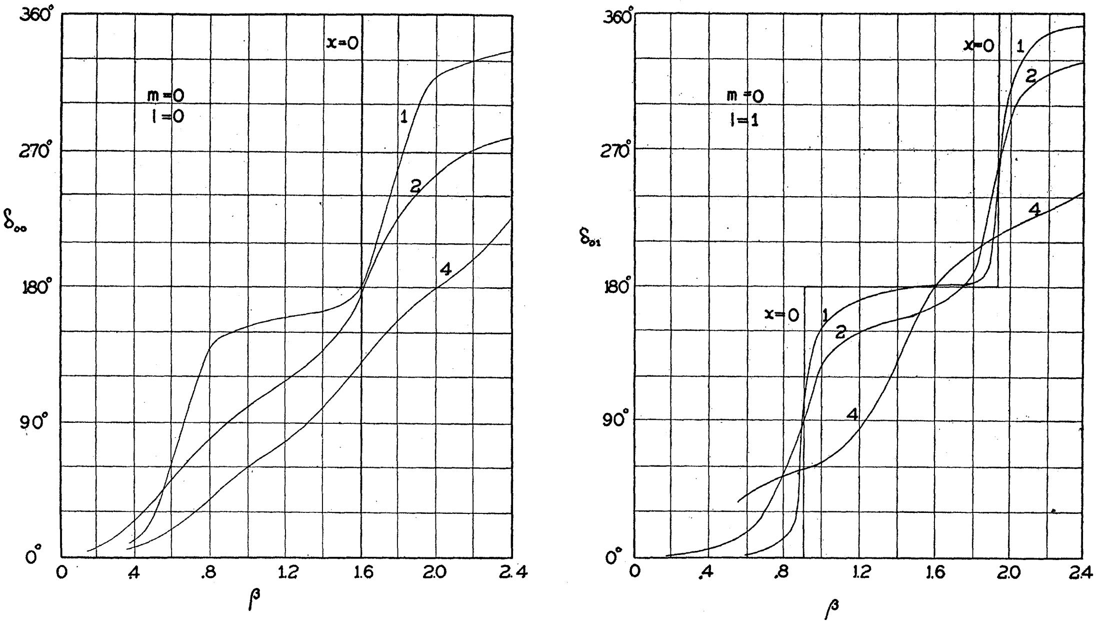
It now remains to identify the molecules with values of β in a consistent manner, and to compare the cross sections in theory and experiment.

5. IDENTIFICATION OF SYMMETRICAL DIATOMIC MOLECULES WITH THE PARAMETER β

Fig. 9 indicates the method used to determine the effective charge number. The light line is that calculated from the empirical rules of Slater,[3] where the electrons of any shell are considered as forming a uniform charge distribution over a surface whose radius is calculated to give best agreement with spectroscopic properties. The dotted line is that of Allis and Morse[1] where $rV(r)$ has been plotted against r such that the lines enclose equal areas. The curved line has been obtained by plotting

$$[(\xi^2-\eta^2)/\xi]V(\xi, \eta)$$

against ξ for $\xi_0=2$, and adjusting Z such that



FIGS. 7 AND 8. "Phase defect," δ_{ml}, as function of for different electron velocities.

again the area under this curve equals that under the broken line.

One must correct finally for the additional positive charge introduced by the potential function. From the previous calculations of F one obtains

$$Z^* = Z_0^*/(1+1.48).$$

The internuclear distances are known from band spectra or from crystal structure. One has, therefore, a definite β for each molecule.

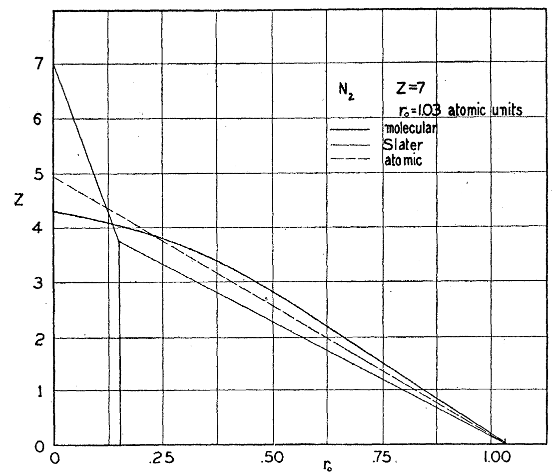


FIG. 9. Method for determination of effective charge number. Plot of V/V (coulomb) as a function of ξ.

6. INTERPRETATION OF EXPERIMENTAL RESULTS

Ramsauer and Kollath,[6] Brüche,[7] Brode,[8] and others, have carried out experiments to obtain the total cross section for elastic scattering in N_2, O_2, and H_2. Fig. 10 shows the structure and final value of Q for N_2, with the experimental results of Brüche for comparison. Apart from the general agreement in shape, position of maxima, and the magnitude of the total cross section as a function of $(\text{volts})^{\frac{1}{2}} \sim x$, it is interesting to note that the theoretical results predict a "fine structure" at about $3.45(V)^{\frac{1}{2}}$. There seems to have been some uncertainty in the experiments regarding this portion of the curve which is generally shown with dotted lines. Of further interest, theory predicts a finite value of Q as $x \rightarrow 0$. It also gives the correct magnitude of Q for large values of x. The experimental difficulties in the range 0 to 1 volt are great, hence, the agreement cannot be pushed in this region.

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[6] Ramsauer and Kollath, *Handbuch der Physik*, Vol. 22, second edition.

[7] Brüche, Ann. d. Physik **4**, 387 (1930); **83**, 1065 (1927). Also, Ergeb. d. ex. Naturwiss. **8**, 185 (1929).

[8] Brode, Rev. Mod. Phys. **5**, 257 (1933).

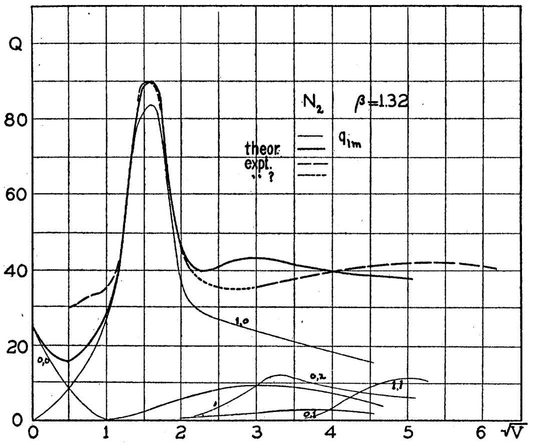

Fig. 10. Total cross section for elastic scattering in N_2 as function of electron velocity in (electron volts)$^{\frac{1}{2}}$. The fine lines are the "partial cross sections."

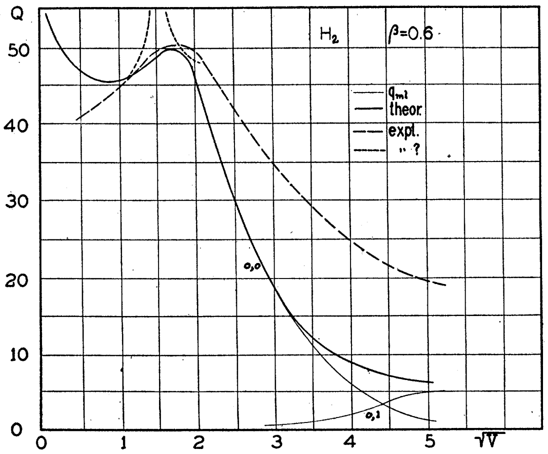

Fig. 12. Total cross section for elastic scattering in H_2.

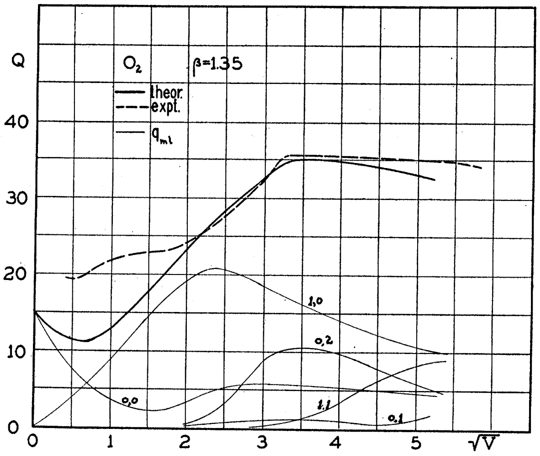

Fig. 11. Total cross section for elastic scattering in O_2.

One might expect to correlate the peak of the cross section curve with the internuclear distance in some manner. No simple correlation has been found for these small velocities. The curve for O_2, Fig. 11, in which there is no sharp peak seems to dismiss the possibility of such a correlation. For low velocities the theory predicts a smaller cross section than that observed. Experimentally, oxygen is a difficult gas with which to work, while low velocity electrons are difficult to obtain. Hence, the agreement may be considered as being good.

Fig. 12 compares the results for H_2. The peaks, magnitude, and general shape agree fairly well. As the velocity of the incident electrons increases, the calculated cross section falls below the experimental value. This is, doubtless, due to the fact that the calculations include only elastic collisions, whereas the experiments necessarily include some inelastic scattering and energy going into excitation and rotation. The energy of excitation of H_2 being low renders this explanation plausible.

Calculations for other molecules, Cl_2, etc., can be made quite readily when there is experimental data for comparison.

The fundamental idea and suggestion for this work come from Professor P. M. Morse. It is a pleasure to acknowledge this and the benefit derived from many interesting discussions and helpful suggestions on the subject.