

Extrapolation of Electron-Rare Gas Atom Cross Sections to Zero Energy*†

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Modified effective-range formulas recently developed for electron-atom scattering are employed first to analyze the Ramsauer-Kollath (RK) electron-rare gas atom cross sections, and then to compare them with determinations of the same quantities made by different and newer methods. It is found that these cross sections can be extrapolated unambiguously down to zero energy. The extrapolated RK scattering lengths are found to be approximately 1.19, 0.24, -1.70 , -3.7 , and $-6.5a_0$ for He, Ne, Ar, Kr, and Xe, respectively. Good agreement is found, in general, both in sign and magnitude with the pressure shift estimates of the scattering lengths. Momentum transfer cross sections are also extended down to zero energy and are compared with some drift velocity and microwave results. The best agreement is found with the Gilardini and Brown curve for Ne, and with those of Pack, Phelps, Frost, and Voshall for the other rare gases, although there are some differences with the latter. In particular, a "pressure effect" is discussed in connection with these results.

I. INTRODUCTION

THIS paper is concerned with the problem of the elastic scattering of electrons from the five rare gases (He, Ne, Ar, Kr, and Xe) in the energy region from zero to several eV. This is a problem which has been attacked experimentally by many different investigators and by a variety of different methods. The total scattering cross sections were studied extensively by direct methods during the late twenties.¹⁻³ Of these investigations, the most thorough were those of Ramsauer and Kollath (RK),^{2,3} whose measurements extended in energy as low as a sixth of a volt, and who studied the differential cross sections at slightly higher energies. An indirect method, that of pressure shifts, was devised by Fermi⁴ and employed by a number of experimenters⁵ during the thirties to estimate the scattering lengths. The more recent investigations⁶⁻¹³ of

the electron-rare gas cross sections have been done by microwave and drift velocity measurements of the electron mobility, mostly in the thermal energy region.

If one looks for agreement or disagreement between the cross sections determined by these different methods, it is found that it has never been possible to compare them quantitatively, mainly because they cover different portions of the energy region (zero, thermal, and eV energies). It is here that the possible value of effective range theory is evident. What effective range theory says in effect is that the scattering amplitude in a certain energy region (here the region from zero to several eV) is completely determined to a certain accuracy by a small number of parameters; and so, in principle just a few experimental points, anywhere in the region, are sufficient to determine the amplitude over the entire region. Thus, effective range theory is the simplest consequence of considering the scattering amplitude as an analytic function of the energy. Now it has been shown¹⁴ that the unusual effective range formulas are not valid for electron-atom scattering, because of the $1/r^4$ polarization interaction at long distances. This reflects the fact that the analytic function in this case has a branch point at the origin.¹⁵ Fortunately, it has been possible to work our modified effective range formulas,^{16,17} applicable to scattering of a charged particle by a neutral polarizable system. These might be called "atomic effective range formulas."¹⁸ In the paper we shall employ these formulas to analyze the RK scattering experiments. In particular,

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² C. Ramsauer and R. Kollath, Ann. Physik 3, 536 (1929).

³ C. Ramsauer and R. Kollath, Ann. Physik 12, 529 and 837 (1932).

⁴ E. Fermi, Nuovo Cimento 11, 157 (1934).

⁵ C. Füchtbauer, P. Schulz, and A. F. Brandt, Z. Physik 90, 403 (1934); C. Füchtbauer and F. Gössler, *ibid.*, 93, 648 (1935); C. Füchtbauer and H. J. Reimers, *ibid.* 95, 1 (1935); T.-Z. Ny and S.-Y. Ch'en, Phys. Rev. 51, 567 (1937).

⁶ A. V. Phelps, O. Fundingsland, and S. Brown, Phys. Rev. 84, 559 (1951).

⁷ L. Gould and S. C. Brown, Phys. Rev. 95, 897 (1954).

⁸ J. M. Anderson and L. Goldstein, Phys. Rev. 102, 933 (1956).

⁹ A. Gilardini and S. C. Brown, Phys. Rev. 105, 31 (1957).

¹⁰ J. C. Bowe, Phys. Rev. 117, 1416 (1960).

¹¹ A. V. Phelps, J. L. Pack, and L. S. Frost, Phys. Rev. 117, 470 (1960).

¹² J. L. Pack and A. V. Phelps, Phys. Rev. 121, 798 (1961).

¹³ J. L. Pack, R. E. Voshall, and A. V. Phelps, Phys. Rev. 127, 798 (1962).

¹⁴ L. Spruch, T. F. O'Malley, and L. Rosenberg, Phys. Rev. Letters 5, 347 (1960).

¹⁵ Roger G. Newton, J. Math. Phys. 1, 344 (1960). The polarization potential is a special case of Yukawa-type potentials with $\mu=0$ and $\rho(\alpha)\sim\alpha^3$ as $\alpha\rightarrow 0$. The branch point however disappears for scattering in the forward direction, a fact which was used by E. Gerjuoy and N. A. Krall, Phys. Rev. 119, 705 (1960) in applying dispersion relations to electron-atom scattering.

¹⁶ T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. 2, 491 (1961).

¹⁷ T. F. O'Malley, L. Spruch, and L. Rosenberg, Phys. Rev. 125, 1300 (1962).

¹⁸ It was from an attempt to find experimental confirmation for these formulas that this research arose. The result has been more an extension of the experimental cross sections than a confirmation of the formulas although there has been some of the latter.

the parameters of the theory will be chosen to fit the experimental cross sections. The result is an extrapolation of the results to zero energy. It then becomes possible to compare these extrapolated results with the pressure shift estimates near zero energy and with the drift velocity cross sections in the thermal region.

This method of analysis might be characterized as a short circuiting of the procedure used by Holtzmark¹⁹ in his remarkable analysis of the Ramsauer cross sections for argon and krypton. Holtzmark added to the Hartree charge distribution of the atoms an "empirical" polarization potential with a variable effective cutoff parameter. By integrating the resulting radial equation by hand and varying the cutoff parameter, he was able to match the experimental cross sections fairly closely. What the present analysis does is to put the variable parameters directly into the phase shifts or the cross sections themselves.

In Sec. II, we briefly recapitulate the formulas of atomic effective range theory for the phase shifts, together with other relevant formulas. The simplest and most striking application of these formulas is to the Ramsauer-Townsend effect. This is the subject of Sec. III, where it is shown that the scattering length is very simply related to the energy of the minimum. Another simple relation is found between this energy and that for the minimum in the momentum transfer cross section. In Sec. IV, we report the results of a detailed fitting of the RK cross sections for all five rare gases, and the resulting analytic expressions for the phase shifts. In Sec. V, the extrapolated RK scattering lengths are compared with those found in the pressure shift experiments (which also require a slight extrapolation). Some comparison is made in Sec. VI with momentum-transfer cross sections found by a number of drift velocity and microwave experiments. Section VII is a brief summary and discussion of the results.

II. SUMMARY OF PERTINENT FORMULAS

We first write for reference the well-known partial-wave expansions for the total scattering cross section,²⁰ σ_S , and the less well known momentum transfer cross section, σ_M .¹⁰ (This cross section controls the diffusion of electrons in gases and, thus, is what is found by modern drift velocity experiments.) The expansions are

$$\sigma_S = (4\pi/k^2) \sum_{L=0}^{\infty} (2L+1) \sin^2(\eta_L), \quad (2.1)$$

$$\sigma_M = (4\pi/k^2) \sum_{L=0}^{\infty} (L+1) \sin^2(\eta_L - \eta_{L+1}), \quad (2.2)$$

where $k^2 = (2m/\hbar^2)E$. It might be pointed out in passing that while the Ramsauer-Townsend minimum occurs in σ_S when $\eta_0 \cong 0 \pmod{\pi}$ at very low energy, it will occur in σ_M when $\eta_0 - \eta_1 \cong 0$. This is discussed further in Sec. III.

¹⁹ J. Holtzmark, *Z. Physik* **66**, 24 (1930); **55**, 437 (1929).

²⁰ The cross sections σ_S and σ_M are related to the corresponding quantities P_S or P_M , the probability of collision at 0°C and 1 mm Hg, by $\sigma/a_0^2 = 1.01P$ (cm⁻¹). See reference 24, p. 2.

The atomic effective range formulas found in reference 17 for electron-atom scattering phase shifts may be written

$$\tan \eta_0 = -Ak - (\pi/3a_0)\alpha k^2 - (4/3a_0)\alpha A k^3 \ln(ka_0) + O(k^3), \quad (2.3a)$$

$$\tan \eta_1 = (\pi/15a_0)\alpha k^2 - A_1 k^3 + O(k^4), \quad (2.3b)$$

$$\tan \eta_L = \pi[(2L+3)(2L+1)(2L-1)a_0]^{-1} \times \alpha k^2 + O(k^4), \quad (L > 1) \quad (2.3c)$$

where a_0 is the electron Bohr radius and α is the electric polarizability of the atom. The numerical values of α for the rare gases are 1.36, 2.65, 11.0, 16.6, and 27.0 a_0^3 for He, Ne, Ar, Kr, and Xe, respectively.²¹ It was seen that these formulas apply to any neutral atom not possessing a permanent electric quadrupole moment (approximately half the atoms in the periodic table). The energy region in which these formulas are applicable is limited, for any L , by the necessary condition that the k^2 term in the appropriate Eq. (2.3) be small compared to unity.²²

It should be noted that $\tan \eta$ on the left-hand side of Eqs. (2.3) could be replaced by $\sin \eta$ or even by $\eta \pmod{\pi}$, and the expansions remain valid to the order in k to which they are written (only higher order terms are changed). In the course of the paper, these alternate forms for Eqs. (2.3) will sometimes be used. With this in mind, let us substitute Eqs. (2.3) into Eqs. (2.1) and (2.2), to obtain the low-energy expansion of σ_S and σ_M . The result is

$$\sigma_S = 4\pi[A^2 + (2\pi/3a_0)\alpha A k + (8/3a_0)\alpha A^2 k^2 \ln(ka_0) + Bk^2 + \dots], \quad (2.4)$$

$$\sigma_M = 4\pi[A^2 + (4\pi/5a_0)\alpha A k + (8/3a_0)\alpha A^2 k^2 \ln(ka_0) + Ck^2 + \dots], \quad (2.5)$$

for k sufficiently small. The parameter B could be expressed in terms of r_{p0} (modified effective range), α , and A , while C involves A_1 as well. For the purposes of this paper, they are considered simply as parameters to be determined by experiment. Notice that both cross sections have the same zero-energy limit, but that σ_M has a steeper slope.

For the sake of completeness, we will also put down the expansion of the differential cross section through powers in $k^2 \ln(ka_0)$, although the straightforward phase-shift analysis will generally be more useful. The expansion is

$$\sigma(\theta) = A^2 + (\pi/a_0)\alpha A k \sin(\theta/2) + (8/3a_0)\alpha A^2 k^2 \ln(ka_0) + O(k^2). \quad (2.6)$$

²¹ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (The Clarendon Press, Oxford, 1932).

²² An interesting study of the extent of this energy region for higher L was made for the e^- -H problem by P. G. Burke and H. M. Schey, *Phys. Rev.* **126**, 147 (1962). This work consisted in comparing the predictions of Eq. (2.3c) (with appropriately chosen polarizability) against the solutions found in the 1S-2S-2P approximation.

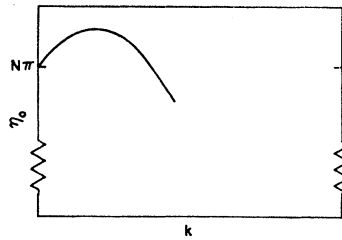


FIG. 1. Behavior of S -wave phase shift in the Ramsauer-Townsend effect.

Equation (2.6) was obtained by substituting Eqs. (2.3) into the general formula for $\sigma(\theta)$ and noting that a certain sum over all the P_L can be done exactly giving $\sin(\theta/2)$. It is interesting to note that the linear k term, peculiar to the long-range force, vanishes in the forward direction. This is related to the fact that the branch cut mentioned previously¹⁵ is not present in the forward scattering amplitude.

III. THE RAMSAUER-TOWNSEND EFFECT

Probably the best known feature of the electron-rare gas atom cross sections is the Ramsauer-Townsend minimum which appears at about half an electron volt in the argon, krypton, and xenon cross-section curves.²³ What is understood theoretically about this effect is summed up by Massey and Burhop.²⁴ The essential features are that the S -wave phase shift is equal to some positive multiple of π at zero energy and that the scattering length must be negative. The phase η_0 , consequently, begins to rise as the energy increases above zero as in Fig. 1; then it must quickly reach a maximum and fall back through the same multiple of π , while the higher partial waves are still small. The result is the nearly vanishing cross section which has been observed.

Now consider the first two terms on the right-hand side of Eq. (2.3a) for the S -wave phase shift. We will show that they are quite adequate to describe, at least qualitatively the observed Ramsauer-Townsend effect. The analysis of the next section will confirm further that they also give quite accurate numbers for the atoms in question. This equation may be written at sufficiently low energy

$$\eta_0 \cong -Ak - (\pi/3a_0)\alpha k^2 \quad (3.1)$$

mod π . If A is a positive number (as it will be seen to be for He and Ne), η_0 will simply decrease monotonically. If, however, A happens to be negative, the phase shift will behave in exactly the manner described above (Fig. 1). There will be an initial increase in the phase followed by a maximum and a passage through zero as

²³ Recently, another case of the Ramsauer-Townsend effect has been found theoretically for the problem of positron scattering by atomic hydrogen at a few eV (assuming that the P -wave phase shift will not be large). See reference 34.

²⁴ H. S. W. Massey and E. H. S. Burhop, *Electron and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1951), p. 113 ff.

the two terms become equal. The energy range during which all this takes place will be determined by the relative magnitudes of A and α . In fact, by setting the right-hand side of Eq. (3.1) equal to zero we find, to first approximation, an extremely simple relation between the scattering length, A , and the energy, E_s , of the scattering cross section minimum (with wave number k_s), namely,

$$A \cong -(\pi/3a_0)\alpha k_s. \quad (3.2)$$

This relation would be exact in the limit of small k_s . We may use it, together with Ramsauer and Kollath's determination of the energy k_s , to determine A at least to a first approximation. The minima were found by RK to lie approximately at 0.37, 0.60, and 0.65 eV for Ar, Kr, and Xe, respectively, giving $k_s = 0.164, 0.209, 0.218 a_0^{-1}$. Substituting these values, together with the known polarizabilities (11.0, 16.6, and $27.0 a_0^3$), into Eq. (3.2), we find immediately

$$A \cong -1.9, -3.7, -6.2 a_0$$

as first approximations for the argon, krypton, and xenon scattering lengths. It is seen in the next section that values are very close to those which follow from a fitting of the detailed cross section curves.

Minimum in Momentum Transfer Cross Section

It might be guessed that the Ramsauer-Townsend minimum should occur at approximately the same place in both scattering and momentum transfer cross sections. A reason for this expectation might be the fact that the two cross sections become identical when phases higher than the S wave are neglected, combined with the assertion that higher order phases are negligible at the Ramsauer-Townsend minimum. However, such reasoning can be misleading since, for example, Eqs. (2.1) and (2.2) show that while η_1 appears only to second order in σ_s , it is a first-order effect in σ_M . In fact, it is shown below that there should be a significant difference in the location of the two minima, especially in the limit of small energies.

According to Eq. (2.2), σ_M will have its minimum approximately when $\eta_0 - \eta_1 = 0 \text{ mod } \pi$, at an energy E_M with an associated wave number k_M . Using Eqs. (2.3a) and (2.3b) for η_0 and η_1 , we find to the same approximation as above (neglecting terms beyond k^2)

$$\eta_0 - \eta_1 \cong -Ak - (2\pi/5a_0)\alpha k^2, \quad (3.3)$$

and, setting this equal to zero,

$$A \cong -(2\pi/5a_0)\alpha k_M. \quad (3.4)$$

Comparing Eqs. (3.4) and (3.2) we find the desired relation between the two minima, namely, $k_M \cong (5/6)k_s$, or

$$E_M/E_s \cong 25/36, \quad (3.5)$$

for E sufficiently small. For the case of argon, the value of E_M has been investigated by Frost and Phelps²⁵ and found to be approximately 0.25 eV as compared with Ramsauer and Kollath's reported value of 0.37 eV for E_S , in surprisingly good agreement with Eq. (3.5). Measurements of E_M for Kr and Xe do not seem to have been completed as yet.²⁶

The Vanishing of η_1

If one looks closely at the RK angular distribution curves,³ it can be seen that there is an analog of the RT effect which occurs in the P -wave phase shift for all the rare gases but He. It appears that the P -wave phase shift for all these gases vanishes somewhere between 1 and 1.5 eV. A closer analysis of these angular distributions, using Eq. (2.3c) for the higher waves,²⁷ indicates that the energies (which we denote as E_1) lie at approximately 1.5, 1.1, 1.0, and 0.8 eV for Ne, Ar, Kr, and Xe, respectively. This information together with Eq. (2.3b) for η_1 can be used exactly as above to determine the quantity A_1 in the P -wave phase shift. In place of Eq. (3.2) one finds

$$A_1 \cong (\pi/15a_0)\alpha k_1^{-1}; \quad (3.6)$$

hence, for these four atoms,

$$A_1 \cong 1.66, 8.0, 12.8, 23.2 a_0^3 \quad (3.7)$$

for Ne, Ar, Kr, and Xe, respectively. The absence of this effect in He is not surprising because the zero-energy limit of η_1 is believed to be zero²⁸ for He while it is at least π for all the other rare gases; thus, if the He phase shift were to pass down through zero it would indicate a repulsive interaction.

With the determination of the parameter A_1 for the four heaviest rare gases, the right-hand side of Eq. (2.3b) for η_1 is completely determined for these atoms, and so the P -wave phase shifts may be considered known, in the light of effective range theory, for the energy range from zero up to several eV. For the higher partial waves ($L > 1$), since the right-hand side of Eq. (2.3c) is very small throughout this energy region, we expect that the approximation it gives for η_L should be good. With the exception of He, then, we are now in

the position of knowing all the phases except the S wave in the energy region from zero to several eV. For Ar, Kr, and Xe, in fact, Eq. (3.1) with the subsequent estimate of A could be taken to complete our knowledge of the phase shifts, at least up to the minimum. However, we shall try in the next section by fitting the detailed RK measurements at the lowest energies to get a more accurate (2 parameter) representation of the S -wave phase shifts which at the same time includes Ne. The He cross sections will then be analyzed separately using Eqs. (2.4) and (2.5).

IV. DETAILED EFFECTIVE RANGE FITTING OF RAMSAUER-KOLLATH CROSS SECTIONS

Ne, Ar, Kr, and Xe

Our procedure in this section will be essentially to substitute the effective range formulas Eqs. (2.3) into Eq. (2.1) for the total scattering cross section, σ_S , and then attempt to choose the undetermined parameters in such a way as to match the experimentally determined RK points at the lowest measured energies. Since the parameter A_1 was determined in the previous section for these four gases, so that the partial cross sections for $L > 0$ are considered to be already known from zero to several eV, there remains only to determine the parameters in the S wave.²⁹ For our present purpose it is most convenient to write Eq. (2.3a) in terms of the sine.³⁰ It becomes simply

$$\begin{aligned} (\sin \eta_0)/k = & -A - (\pi/3a_0)\alpha k \\ & - (4/3a_0)\alpha A k^2 \ln(ka_0) + Dk^2 + \dots \end{aligned} \quad (4.1)$$

There are then two free parameters, A and D , which we are to choose so as to give the best fit to the experimental points. As mentioned earlier, the applicability of the expansions for the S wave is expected to be limited to the region where the second term in Eq. (2.3a) is small compared to unity. For neon this region extends up to a couple of eV, while for the heavier gases it reaches to the neighborhood of the minimum. This takes in six or seven experimental points in the case of Ar and Kr, but only two to three for Xe. The best fits to the data give scattering lengths which for the three heavy rare gases are very close to those determined more approximately in the last section. They are

$$A = 0.24, -1.70, -3.7, -6.5 a_0 \quad (4.2)$$

for Ne, Ar, Kr, and Xe, respectively.

The analytic expressions for the respective phase

²⁵ L. S. Frost and A. V. Phelps, Bull. Am. Phys. Soc. 5, 371 (1960).

²⁶ We have been informed that preliminary investigations by Phelps *et al.* seem to indicate that, at least for Xe, E_M will not differ very much from E_S . This is probably related to the fact that the phase shift, η_1 , which is responsible for the difference between E_S and E_M , passes through zero very soon after η_0 for Xe (see next subsection), and so Eq. (3.3) is really too drastic an approximation in this case.

²⁷ To the extent that the partial waves for $L=3, 5, \dots$ are negligible, the vanishing of η_1 will make the angular distributions symmetrical about 90° . However, for the rare gases at the energies in question, these phase shifts, though very small, do have a noticeable effect. Hence, a more careful analysis has to be done to determine just where η_1 vanishes.

²⁸ See reference 24, p. 118.

²⁹ This procedure differs from that used in deriving Eqs. (2.4) and (2.5), where like terms were combined and all terms higher than quadratic were finally dropped. Here the different partial waves are treated independently.

³⁰ When written for the sine rather than the tangent, the formulas are determined only to within a factor of ± 1 , essentially because $\sin(x+n\pi) = \pm \sin(x)$. We have chosen the sign to agree with that of the tangent.

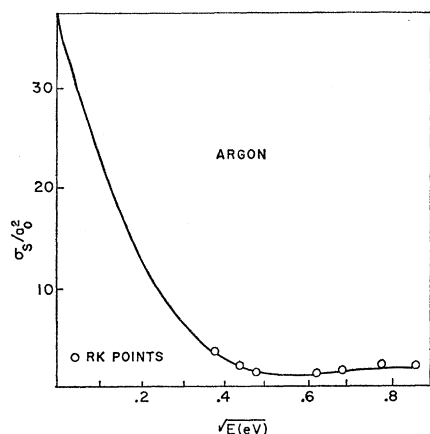


FIG. 2. Total scattering cross section for electrons on argon, plotted against the square root of the energy. The solid curve represents the effective range fit found in this paper to the Ramsauer-Kollath experimental points.

shifts were found to be

$$\begin{aligned} (\text{Ne}) \quad (\sin\eta_0)/k = & -0.24 - 0.756E^{1/2} \\ & - 0.031E \ln E + 0.317E, \quad (4.3a) \end{aligned}$$

$$\begin{aligned} (\text{Ar}) \quad (\sin\eta_0)/k = & 1.70 - 3.13E^{1/2} \\ & + 0.92E \ln E + 1.23E, \quad (4.3b) \end{aligned}$$

$$\begin{aligned} (\text{Kr}) \quad (\sin\eta_0)/k = & 3.7 - 4.74E^{1/2} \\ & + 3.01E \ln E + 1.84E, \quad (4.3c) \end{aligned}$$

$$\begin{aligned} (\text{Xe}) \quad (\sin\eta_0)/k = & 6.5 - 7.68E^{1/2} \\ & + 8.58E \ln E + 6.10E, \quad (4.3d) \end{aligned}$$

where E , the energy in eV, is related to k by $E = 13.6 (ka_0)^2$ eV. The total scattering cross sections, σ_s , determined from these expressions, together with Eqs. (2.3b), (3.7), and (2.3c) for the higher partial waves, are plotted in Figs. 2, 3, and 4.

The fit for Ar and Kr is seen to be especially good. The fact that so many points are matched accurately

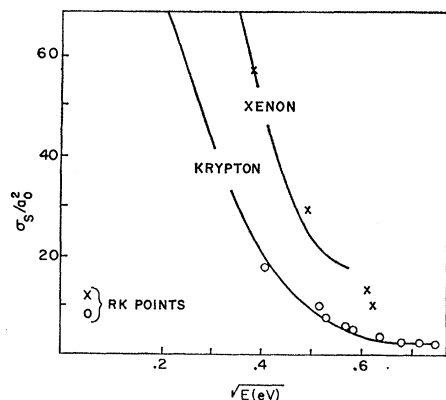


FIG. 3. Total scattering cross sections for electrons on Kr and Xe. Experimental points together with their effective range fit.

by the two parameter curves would seem to be a good consistency check on the RK experiments and also, to some extent, a vindication of the theory. For Xe there are too few points in the energy region for such consistency, although the closeness of the scattering length to that found by matching a different point (the minimum) in the last section is encouraging.

There are two noticeable features of the Ne curve, Fig. 4. The first is that all the experimental points below 1 eV lie more or less on a straight line when plotted against the square root of the energy. This makes the RK neon results probably the only clear experimental example of the linear $E^{1/2}$ behavior of the low-energy scattering³¹ cross sections predicted by the theory [see, e.g., Eq. (2.4)]. The second feature is a negative one. It will be noticed that the best fit which the theory with two parameters could give to the experimental Ne points is a sort of average about which the experimental points oscillate somewhat. The same effect appears in a more pronounced way in the helium curve and is discussed in connection with the He results.

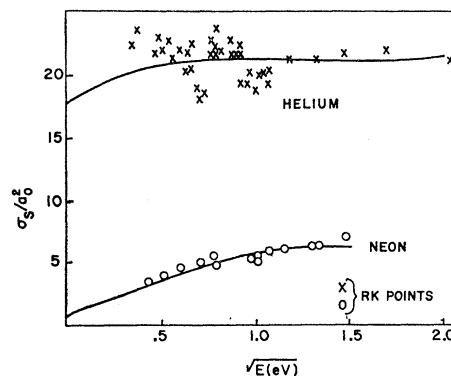


FIG. 4. Total scattering cross sections for electrons on He and Ne. RK experimental points together with their effective range fit.

This finishes our analysis of the RK electron scattering cross sections for Ne, Ar, Kr, and Xe. It should be pointed out that, since we have obtained each phase shift separately, the momentum transfer cross sections, σ_M , are also determined (see Sec. VI), as well as the differential cross sections.

Helium

Up to now, helium has been omitted from the analysis. The reason is that the P -wave phase shift was not found to pass through zero at low energies and so its parameter, A_1 , could not be determined by the simple procedure of the last section. However, the cross sections taken as a whole (both σ_s and σ_M) can be expanded according to Eqs. (2.4) and (2.5). The

³¹ The same is also true of the Gilardini and Brown curve, reference 7, for the momentum transfer cross section.

parameters in Eq. (2.4) for σ_S are then chosen to fit the RK total scattering cross section. The momentum transfer cross section, σ_M , is matched to that deduced by Barbieri³² from the RK angular distributions. The same scattering length is found in matching both sets of data (which are not really independent), namely,

$$A(\text{He}) = 1.19 a_0. \quad (4.4)$$

The analytical curves chosen according to Eqs. (2.4) and (2.5) which give the best fit to the experimental points in the energy domain appropriate for He (up to about 5 eV) are

$$\sigma_S/a_0^2 = 17.8 + 11.4E^{1/2} + 2.36E \ln E - 7.98E, \quad (4.5)$$

$$\sigma_M/a_0^2 = 17.8 + 13.7E^{1/2} + 2.36E \ln E - 8.57E. \quad (4.6)$$

The scattering cross-section curve, σ_S , is plotted in Fig. 4 together with the RK points which it was chosen to match. (See Sec. VI for σ_M .) It is noticed that the experimental points exhibit what Ramsauer called a "fine structure" below 1.5 eV. Equation (2.4) is not compatible with such a fine structure. The closest fit which can be made using it is a cross section which is essentially constant through the entire experimental region, taking on an average value of the experimental points, and which decreases somewhat as the energy approaches zero. [It should be pointed out that this decrease in the cross section near zero energy is a necessary consequence of the second term in Eq. (2.4).]

This "fine structure" in the RK He cross section is the only serious problem encountered in analyzing these data. For a number of reasons it is very difficult to believe that the fine structure could be a property of the actual He-electron cross section. Both experiment³ and theory³³ indicate that the higher phase shifts are almost negligibly small below 2 eV, so that the structure would have to come from the S wave. Now there has never been any mechanism suggested which might account for such fine structure in the S -wave phase shift. What calculations have been done on He,³³ together with the very precise electron-hydrogen calculations,³⁴ tend to indicate that η_0 should vary smoothly, even monotonically.

If, then, the observed fine structure is not considered to be a property of the actual He cross section, it must be regarded as a spurious effect of some sort. It might be explained, for example, by the small random errors which one expects in an experiment. However, the large number of points involved and the very systematic movement which they show would seem to make this explanation unlikely. This leaves the possibility that some systematic source of error is responsible for the maxima and minima. The most likely systematic error would seem to be the presence of a small amount of impurity in the helium. If it is assumed that this is so,

TABLE I. Electron-rare gas atom scattering lengths (in Bohr radii), extrapolated from different experiments.

	He	Ne	Ar	Kr	Xe
RK	1.19	0.24	-1.70	-3.7	-6.5
Pressure shift ^a	1.12	0.14	-1.40	-3.1	-5.7
Pressure shift ^b	1.06	0.03	-1.86	-3.8	-6.9
PFB	1.14	0.39		-3.2	-5.6
Other microwave	1.19 ^c	0.18 ^d			
PVP, PP	1.15 ^e		-1.69	-3.2	-6.0

^a Uncorrected, reference 36.

^b Extrapolated to zero energy.

^c Gould and Brown, reference 7.

^d Gilardini and Brown, reference 9.

^e See reference 41 (also 42).

then a good part of the fine structure, particularly the sharp minimum at 1 eV, can be explained by the presence of a few percent of N_2 in the helium.³⁵ The hypothesis of an N_2 impurity is strengthened somewhat by the fact that the RK cross section for Ne seems to show a similar structure with a minimum at 1 eV, although there are fewer points involved, for Ne and the effect tends to be obscured by the slope of the Ne curve below 1 eV.

Rather than actually subtract off the supposed effect of the impurities and calculate what might be a better estimate of the true He cross section, we have thought it better to extrapolate the actual RK (average) cross section as it was found and to let further refinements await more accurate experiments. This closes our analysis of the RK results. In the following sections we shall compare these extrapolations with other experimental results especially in the limit of zero energy.

V. SCATTERING LENGTHS DETERMINED BY PRESSURE SHIFT METHOD

Indirect measurements of the electron-rare gas atom scattering lengths were made during the thirties,⁵ using a method due to Fermi,⁴ that of pressure shifts. This method, a summary of which can be found in Massey and Burhop's book,³⁶ relates the scattering length to the shift caused in the energy of highly excited alkali atoms when these atoms are perturbed by a small quantity of the gas in question. The effect is observed as a shift in the spectral lines associated with the states of high principle quantum number, n .³⁷

In the second row of Table I, are listed the scattering lengths found by the pressure shift experiments,³⁸ which

³⁵ Some numerical work done on this assumption indicates that subtracting out the effect of a 3% impurity of N_2 and also a comparable amount of O_2 has the effect of removing the largest part of the systematic fine structure from the RK curve. The cross section, which is thereby reduced by between 10 and 20%, can then be fitted by Eq. (2.4) much more closely than the original cross section. The scattering length is found to be approximately $1.13a_0$.

³⁶ See reference 24, p. 178, ff.

³⁷ These excited states are characterized by a valence electron, practically free, moving in a Bohr orbit of radius n^2a_0 about a positive core, and with wave number $k \cong (na_0)^{-1}$.

³⁸ The table represents the same selection of pressure shift results used in reference 36. For He and Ne, an average of the two values is used.

³² D. Barbieri, Phys. Rev. **84**, 653 (1951).

³³ P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).

³⁴ C. Schwartz, Phys. Rev. **124**, 1468 (1961).

may now be compared with the RK scattering lengths in the first row. However, what was found by these experiments was not quite the scattering length. The theory considers states of the alkalis of principle quantum number n , in the limit as $n \rightarrow \infty$, so that $k = (na_0)^{-1} \rightarrow 0$. In practice, the observations were made for states of n between twenty and thirty, corresponding to thermal energies, and, in general, no extrapolation to $n = \infty$ was attempted.

We should like to extrapolate these results to $n = \infty$ ($k = 0$), although the difference proves to be relatively small. If one looks at the derivation of the relation between pressure shift and scattering length, it will be recognized that the contribution to the shift coming from the electron-rare gas atom interaction follows almost immediately, at zero energy, from the identity for the scattering length

$$A = (2m/\hbar^2) \int V\psi d\tau.$$

The integral on the right is interpreted as a certain average energy for the system ($\langle V\psi \rangle_{av} \cong \bar{V}\psi$), due to the electron-atom interaction V , and averaged over an appropriate region of space. This average energy is seen to be proportional to the scattering length. Now if the energy of the electron is very small, but not exactly zero, we may expect that the energy shift is proportional (at least to first order in k) to the quantity, $-(\tan\eta_0)/k$, of which A is the zero-energy limit. By Eq. (2.3a) this quantity is equal, to first order in k , to $A + (\pi/3a_0)\alpha k$. An extrapolation of the pressure shift results to zero energy is then possible (given the above assumption) by subtracting this linear k term from the reported values of the scattering length. As was mentioned earlier, the wave number of the valence electrons in question is given by $k = (na_0)^{-1}$, and the n values for the experiments lay somewhere between 20 and 30. For simplicity the extrapolation was done with a value of k corresponding to $n = 25$ (0.022 eV) for all five rare gases. (The actual n values were all fairly close to this.)

The corrected pressure shift scattering lengths are listed in row 3 of Table I. If these are compared with the extrapolated RK scattering lengths in row 1, the agreement in general can be seen to be quite good.³⁹ This is taken as lending some weight to both sets of results. The only exception is Ne where the agreement looks poor (although the magnitude of the difference, $0.2a_0$, is not much larger than those for the other atoms). In the next section it will be seen that the results of drift velocity measurements are in much better agreement with the higher RK scattering length. The exceptionally low value of the pressure shift scattering length for Ne seems to indicate a limitation of the accuracy of the pressure shift method. Apparently, the measurements

themselves were fairly precise. A probable source of error lies in a theoretical correction³⁶ which must be made to the experimentally observed frequency shift in order to account for the polarization of the gas atom by the positive alkali cores. This correction, which involves a fairly rough averaging process, is only a small correction for the other rare gases; for Ne, however, where the observed shift is practically zero, this rough correction is the dominant term. The difference between the RK and pressure shift scattering length for He and Ar, while small, is not negligible, while for Kr and Xe the agreement seems extremely good.

VI. COMPARISON WITH DRIFT VELOCITY AND MICROWAVE CROSS SECTIONS AT LOW ENERGIES

In preceding sections, we have used the atomic effective range formulas of I to extrapolate the RK cross sections to zero energy. In the process, the momentum transfer cross sections were determined as well. In the last section it was shown that the zero-energy results are in good agreement with the results of pressure shift experiments. In the present section we wish to compare these scattering lengths and also the extrapolated momentum transfer curves with the results of microwave and drift velocity experiments, which represent the most recent determinations of the low-energy cross sections.

Phelps, Fundingsland, and Brown

Phelps, Fundingsland, and Brown (PFB), studying all five rare gases, used microwave methods to find average momentum transfer cross sections in a small energy region centered about 0.039 eV. In order to compare these cross sections with the extrapolated RK and pressure shift results, it will be most convenient to make an extrapolation of the PFB cross sections to zero energy, so as to obtain a scattering length. This is done most readily by taking the square root of Eq. (2.5) for σ_M

$$\pm (\sigma_M/4\pi)^{1/2} = A + (2\pi/5a_0)\alpha k + \dots \quad (6.1)$$

To apply this formula to the present case, the PFB average cross sections are taken to represent approximately the values of the cross sections at 0.039 eV, the average energy. The sign of the square root, of course, is not given by the PFB experiment. It must be taken, in general, to agree with the sign of the scattering length in the zero-energy limit. For this we have assumed the sign of A measured directly by the pressure shift method, and found independently in extrapolating the RK data. The resulting scattering lengths are plotted in the fourth row of Table I.⁴⁰ Again the agreement with the RK scattering lengths is good, especially if we

³⁹ Actually, the uncorrected values are equally close on the average, the two tending to lie on opposite sides of the RK scattering lengths.

⁴⁰ The argon result is not included because it was subsequently discovered [see reference (12)] that the electrons for this experiment were not in thermal equilibrium. It has also been suggested that the same may be true for Ne.

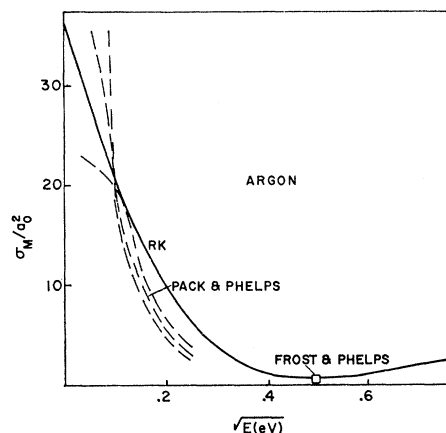


FIG. 5. Momentum transfer cross sections for electrons on argon, plotted against the square root of the energy. The extrapolated Ramsauer-Kollath curve, constructed from the phase shifts found in this paper, is compared with the three two-parameter curves of Pack and Phelps, and with the minimum point of Frost and Phelps.

remember that the extrapolation by Eq. (6.1) is only a first approximation. The result for Ne lends some support to the higher RK scattering length as against the pressure shift result.

Pack and Phelps—Pack, Voshall, and Phelps

The very recent experiments of Pack and Phelps¹² and of Pack, Voshall, and Phelps (PVP)¹³ include all the rare gases except neon. By measuring the drift velocities at two or three different temperatures, the authors were able to deduce two parameters momentum transfer cross-section curves (three for each gas) for the energy region between about 0.003 and 0.08 eV. There are a number of ways in which these experiments could be analyzed in the light of atomic effective range theory, but for the sake of brevity we will only make some simple observations.

First of all these results, just as the PFB cross sections, implicitly contain the scattering lengths. At low enough energies, as was seen, only one experimental point is needed for this purpose together with Eq. (6.1). The fact that the investigators found three different cross sections each for Ar, Kr, and Xe would seem to be a problem. However, in each case, there are two points where the three curves almost exactly come together (see Figs. 5 and 6). Taking the lowest in energy of these points, which lies at approximately 0.012 eV for argon and 0.023 eV for Kr and Xe, we may substitute the value of the cross section into Eq. (6.1) to obtain the scattering length to a first approximation. For He, where only one curve was found, the approximate midpoint (1/40 eV) was used⁴¹ just as with the

⁴¹ Since Pack and Phelps found the helium cross section to be nearly energy independent at thermal energies, the extrapolated He scattering length will be lower than that indicated by their constant cross section. See Discussion in this section on the "pressure effect."

PFB results. The scattering lengths found in this way were 1.15, -1.69, -3.2, -6.0 a_0 for He, Ar, Kr, and Xe, respectively.⁴² These are included in row 6 of Table I from which it can be seen that they are quite close to the RK values.

The methods of this paper might also be used as a means to help remove the ambiguity of the three different curves⁴³ found by these authors for the heavy rare gases, for example by attempting to fit these curves as was done in Sec. IV. However, we shall merely compare these curves with the extrapolated RK curve (see Figs. 5 and 6). We see that, in each case, at energies above 1 or 2 hundredths of a volt it is the highest of the 3 drift velocity curves (called σ_1 by the authors) which lies closest to the RK curve. Perhaps, more significantly, the shape of this curve (σ_1) is closest to that of the RK curve whose shape is determined almost entirely by the theory.

Finally, something should be said about the "pressure effect," or the influence of the gas density on the cross sections, since the experiments involved pressures of up to an atmosphere. As pointed out by Kivel,⁴⁴ the long range nature of the r^{-4} interaction between electron and atom may make the average separation between atoms a relevant parameter near zero energy. Since the distance between electron and nearest atom is never much more than half the average interatomic separation, at distances larger than this the electron will be

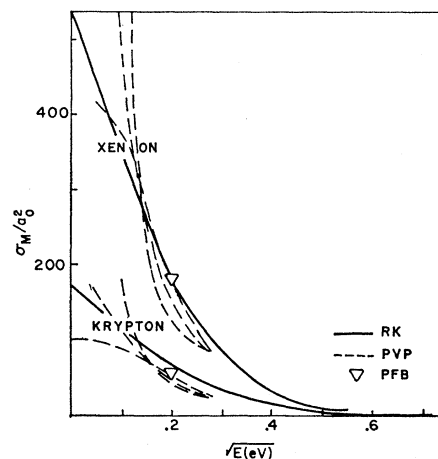


FIG. 6. Momentum transfer cross sections for electrons on Kr and Xe. The results of the present paper are compared with the families of curves found by Pack, Voshall, and Phelps. The average cross sections found by Phelps, Fundingsland, and Brown are also shown.

⁴² A measure of the error introduced by the simple extrapolation process used may be found by evaluating the third and fourth terms in Eqs. (4.3) at the energies in question. The resulting uncertainties are 0.01, 0.03, 0.2, and 0.6 a_0 for He, Ar, Kr, Xe. A similar estimate could also be made in connection with the PFB results above.

⁴³ It has been pointed out to us by Dr. Phelps that this ambiguity in the cross-section curves is now in the process of being removed by studying the ratio, D/μ , of the diffusion coefficient to the mobility.

⁴⁴ B. Kivel, Phys. Rev. **116**, 926 (1959).

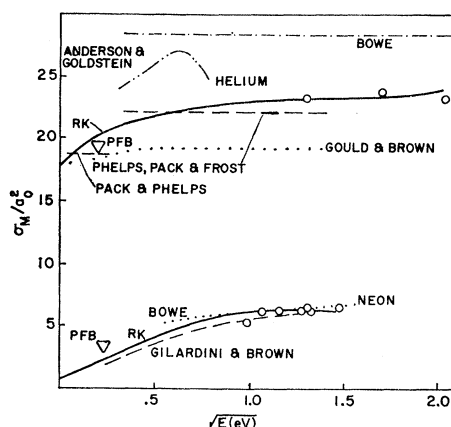


FIG. 7. Momentum transfer cross sections for He and Ne. Various results are compared. The solid curves are the extrapolations of the Ramsauer-Kollath results found in this paper, and the circles are the RK points as analyzed by Barbieri.

interacting with several atoms at once, thus changing the contribution to the cross section from this region of space.

To get a quantitative notion of this effect, consider the contribution to the scattering length due to the polarization potential, $-e^2\alpha/(2r^4)$ from distances greater than R . If R is large, this is given very accurately by the Born approximation, $\Delta A = -\alpha/Ra_0$. At finite energy, the contribution to the S -wave phase shift is similarly found to be $\Delta\eta_0/k = (\alpha/k^2a_0) \int_R^\infty r^{-4} \sin^2(kr) dr$. This has its maximum value ($-\Delta A$) at $k=0$ and falls off rapidly with energy, becoming negligibly small above $kR \cong 1$. For example, if $R=40a_0$, which is of the order of the separations near atmospheric pressure, there should be an uncertainty of 0.04 and 0.27 in the *directly* measured He and Ar scattering lengths, while at finite energy this uncertainty should become negligible somewhat above 0.01 eV.

In the drift velocity experiments, where all the electrons at the higher temperatures and nearly half of those at the lowest temperature were above such an energy, the effect of the pressure on these results should be fairly small in general, even in the low-energy range which they represent. However, such a pressure effect could very well be responsible for the abnormally constant cross section which Pack and Phelps found for helium (see Fig. 7). If one accepts the simple picture proposed by Kivel that the potential seen by an electron is effectively *screened* beyond a distance R determined by the density of the gas, one should then subtract the contribution from this region (as found above) to the phase shift. The effect on the cross section would then be to "round off" the σ vs \sqrt{E} curve, so that it is essentially constant up to $kR \cong 1$ and then smoothly joins the correct curve somewhat above this energy. When less ambiguous curves are found for the heavier rare gases, it should be possible to look for this

effect on them. It should be more pronounced for the heavier rare gases due to their greater polarizabilities.

Helium and Neon Curves

Most of the other drift velocity and microwave experiments which give low-energy cross sections concentrate on the lighter gases, He and Ne. Among these the neon curve found by Gilardini and Brown⁹ (Fig. 7) represents the most clear-cut experimental example of the $E^{1/2}$ dependence of the electron atom cross section required by the theory. The extrapolated RK curve may be seen to be in excellent agreement with this curve, lying just slightly above it. The PFB result⁶ as mentioned is somewhat higher, while the Bowe¹⁰ curve lies close to the RK result in the energy region it covers.

The He curves, which are plotted in Fig. 7, show a diversity of results. It can be seen that the RK curve lies fairly close to the Phelps, Pack, and Frost¹¹ curve in the higher energy range from about 1/10 to 2 eV, while at lower energies it passes down through the Pack and Phelps curve mentioned previously. If these two curves are taken together to indicate a single energy-dependent cross section, as these authors suggest, then the over-all agreement with the RK curve is good, although the difficulty of the lack of slope of the Pack and Phelps curve has already been mentioned. The PFB⁶ value, as was mentioned, lies very close to the RK and Pack and Phelps curves at 1/25 eV, while that of Gould and Brown⁷ is somewhat lower except near zero energy. The Bowe¹⁰ and the Anderson and Goldstein⁸ curves, on the other hand, are consistently higher.

VII. SUMMARY AND CONCLUSIONS

In applying the atomic effective range formulas to the results of experiment, it has been found, first of all, that scattering experiments such as those of Ramsauer and Kollath, which were done down to energies a little below 1 eV, could be extrapolated unambiguously to zero energy, where they could then be compared with various other results. In the course of this analysis it was found that these formulas are very well suited to an analysis of the Ramsauer-Townsend effect. Rough estimates of the scattering length found by the pressure shift method were found to lie fairly close to those extrapolated from the RK experiments, the worst case being Ne where the results differ by $0.2 a_0$. Scattering lengths obtained from an analysis of some later and presumably more precise drift velocity experiments were found to be in good agreement with the two sets of earlier results, so that the scattering lengths may well be determined to within a few percent. In addition to a study of the scattering lengths, a direct comparison was possible between momentum transfer curves derived from the RK results and those inferred from microwave and drift velocity experiments, resulting in

a more coherent picture of these low-energy cross sections.

With the electron-rare gas atom scattering lengths apparently well known, it is tempting to offer a simple model from which they would follow. In a model previously suggested by Kivel,⁴⁵ the effect of the closed electron shells on the scattering was taken to vanish exactly, with the scattering length being determined entirely by the polarization potential. This potential was further assumed to start at a very large distance from the atom. This picture is clearly too simple since it predicts a negative scattering length for all the rare gases, in contradiction to the He and Ne results. (At finite energies it is also inconsistent with the Ramsauer-Townsend effect.) However, if the model is modified so that there is a small positive scattering length of magnitude 1 to $\frac{3}{2} a_0$ contributed by the closed shells in

each case, while the polarization potential begins at a distance of 3 to 4 a_0 (as it does effectively for hydrogen), then all the scattering lengths are predicted accurately. The contribution from the closed shells might then be interpreted as an effectively repulsive core, whose small radius may be thought of as an effective atomic radius.

Finally, there are a number of things which have been left undone, such as a more serious analysis of the drift velocity data, and a detailed study of the differential cross sections.

ACKNOWLEDGMENTS

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⁴⁵ B. Kivel, Phys. Rev. **116**, 1484 (1959).

Further Results Concerning Half-Integral Hylleraas Expansions*

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Previous calculations concerning the ground state of two-electron atoms, involving Ritz-Hylleraas expansions with half-integral powers, are continued through expansions involving 31 parameters. As far as can be judged from a comparison of the energies with those obtained with other expansions, the results continue to be favorable. Thus, already with 18 parameters, the computed energies for He and O VII differ from the best published values by 2 and 0.3 parts per million, respectively. Even better results are obtained for He with expansions involving both half-integral and negative powers. A few initial results of calculations for the excited state 2 ¹S are also presented.

1. INTRODUCTION

THE ground-state solution of the nonrelativistic Schrödinger equation for two-electron atoms has recently received considerable attention. Two problems are of immediate interest: the determination of the energy eigenvalue (of the nonrelativistic Hamiltonian for helium) with an accuracy of better than one part per million (ppm), and the determination of the analytic behavior of the corresponding eigenfunction near the singularities of the wave equation.

The significance of having a solution of the first problem, in view of the recent very careful relevant measurements of Herzberg,¹ is well known.² In all likeli-

hood, the recent very extensive calculational results³ already provide the requisite solution. There still remains a shadow of doubt because the rigorously calculated lower bound of the energy falls short of providing together with the more precise upper bounds, limits of the desired accuracy.⁴

The second problem is of interest both in connection with the first problem (quite obviously so), and also in connection with the search for practically tractable and reliable approximations to the ground-state eigenfunctions of two-electron atoms that can serve as standards of comparison in the current attempts to

* This work was supported in part by the U. S. Atomic Energy Commission.

¹ G. Herzberg, Proc. Roy. Soc. (London) **A248**, 309 (1958).

² For its bearing on the important question of a confirmation of the computed first-order radiative corrections in this two-body problem, see, e.g., reference 1.

³ T. Kinoshita, Phys. Rev. **105**, 1490 (1957); **115**, 366 (1959); C. L. Pekeris, *ibid.* **112**, 1649 (1958); **115**, 1216 (1959); W. Kolos, C. C. J. Rothaan, and R. A. Sack, Rev. Mod. Phys. **32**, 178 (1960); G. Munschy and P. Pluvinaige, J. Phys. Radium **23**, 184 (1962); C. Schwartz, Phys. Rev. **128**, 1146 (1962).

⁴ It is possible, though, to arrive at an adequate lower bound on the basis of reasoning, which, while falling short of absolute rigor, can be taken to possess a high degree of credibility [Bull. Am. Phys. Soc. **5**, 65 (1960)].