

Partial Wave Analysis
Applied to the Ramsauer Effect

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Introduction

In two articles published in 1921, C. Ramsauer reported experimental measurements of the collision cross sections of slow electrons incident upon several noble gases¹. His data was reminiscent of the then recent *ultraviolet catastrophe*. Classic collision theory predicts that the collision cross section should vary inversely with the electron energy. The data, however, was in stark contrast to this understanding. A dramatic local minima, nearing values of zero, was found in the vicinity of electron energy just less than 1 eV. The Ramsauer effect (as it is now referred to) was direct empirical evidence of the wave nature of matter, but it was not recognized as such. It is interesting to note that this phenomenon was made public a full two years prior to the first reported articulation of De Broglie's famous postulate.

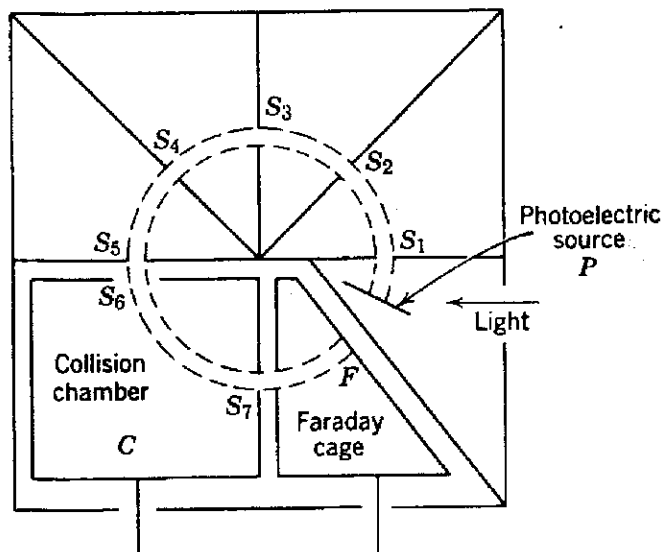


Figure 1: Schematic of Ramsauer apparatus.

The Experiment

Figure 1 shows the schematic representation of Ramsauer's experimental apparatus as presented in his original publication. Electrons were liberated photoelectrically near slit 1. They were then accelerated toward slit 1 by an electrostatic potential. A centripetal acceleration was produced by a magnetic field normal to the plane of the drawing. The remaining seven slits (S2 through S7 plus the entrance to the Faraday cage) ensured a nearly monoenergetic unperturbed electron beam. The target gas molecules were flowed through the collision chamber and the corresponding decrease in current to the Faraday cage was observed.

The finer details of the experiment are unimportant with regard to the topic of this paper. The important point here is that for a given target gas pressure, the current to the Faraday cage was expected to decrease as the electron energy (velocity) decreased. Instead, in the region slightly less than 1 eV, the electron current to the Faraday cage increased dramatically, almost to its unperturbed value. In other words, the collision cross section fell to nearly zero as the target gas molecules became apparently and anomalously transparent to the incident electrons (see figure 2²).

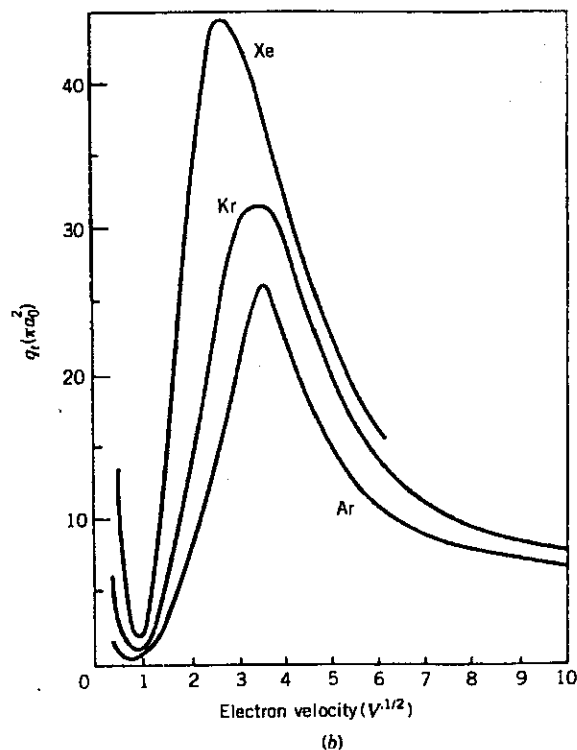


Figure 2 Electron collision cross sections.

Partial Waves and the Ramsauer Minimum

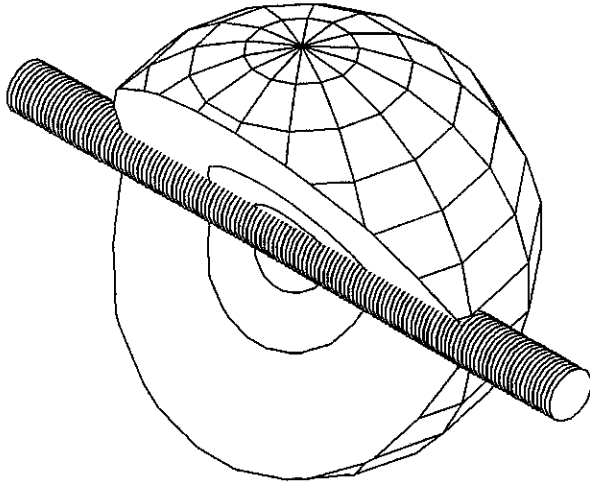


Figure 3: Incident plane waves and scattered spherical waves.

waves are incident upon the region of a scattering force, and spherical waves emanate from the region. There are no contact forces at work, the incident waves are scattered only by interaction with a potential field. Since this paper concerns the Ramsauer effect, scattering is assumed to be the result of elastic collisions. The two fluxes of waves can be expressed by the eigenfunction

$$\Psi(r, \theta) = \psi_i + \psi_s = e^{iKr \cos(\theta)} + \frac{f(\theta)}{r} \cdot e^{iKr} \quad |r \rightarrow \infty \quad (1)$$

a sum of independent incident and scattered wave functions. The eigenfunction is written in spherical coordinates with the origin at the center of the scattering potential. Note that there is complete symmetry in ϕ . Note also that $r \cos(\theta) = z$ and that the first term is just the unnormalized function of a plane wave moving along the z -axis. The second term represents the scattered waves moving in the direction of increasing r with an angular dependence of $f(\theta)$. The r^{-1} factor insures that the scattered waves obey the inverse square law. Finally, note that this eigenfunction is asymptotic. It is offered here without proof that this eigenfunction represents a solution to Schrödinger's time independent wave equation in the limit that r approaches infinity and $V(r) = 0$.

This is consistent with the limitations of the lab perspective. The incident flux of electrons must be measured at some value of r sufficiently large that the r^{-1} term in the scattered flux will render it insignificant. Also, the scattered flux must be measured in regions beyond the transverse limits of the incident flux of electrons. In other words, the measured data will be observed at values of r which, relative to the scale of the scattering potential, approach infinity. Also, the measured data will be observed in a region far from the scattering potential $V(r) \neq 0$.

The incident flux, I , expressed as the probability per second that an electron will impact a space of unit area, is

$$I = v \psi^* \psi = v (e^{iKr \cos(\theta)}) (e^{-iKr \cos(\theta)}) = v \quad (2)$$

There is no interpretation of classical physics which can account for Ramsauer's empirical data. It was truly confounding to the contemporary ideas of particulate matter. To explain it required a wholly new theory, in particular wave mechanics applied to the electron.

A typical electron scattering event can be described as two sustained fluxes of electrons, one incident upon the scattering force and one scattered by that same force. The two fluxes of electrons can each be expressed as an infinite sum of discrete waves, so-called partial waves. One consequence of doing so is an elegant description of precisely the phenomenon observed by Ramsauer.

Figure 3 depicts a set of nodal surfaces which represent a wave scattering event. Plane

where v is the velocity of the electron. The probability that a scattered electron will cross a space of differential area dA is

$$S(\theta) = v \psi^* \psi dA = v \left(f^*(\theta) \frac{e^{-iKr}}{r} \right) \left(f(\theta) \frac{e^{iKr}}{r} \right) dA = v f^*(\theta) f(\theta) \frac{dA}{r^2} = v f^*(\theta) f(\theta) d\Omega \quad (3)$$

Thus, the differential collision cross section is

$$\frac{d\sigma}{d\Omega} = \frac{S(\theta)}{I} = \frac{v f^*(\theta) f(\theta)}{v} = f^*(\theta) f(\theta) \quad (4)$$

and the collision cross section is

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int f^*(\theta) f(\theta) d\Omega \quad (5)$$

Therefore, to evaluate the collision cross section of a scattering event, it is necessary to determine $f(\theta)$.

The details of decomposing $\Psi(r, \theta)$ into a set of partial waves are involved, but not difficult. They are very similar to the same exercises every physics graduate student has done in his or her quantum mechanics courses. In lieu of revisiting the exercise here, the reader is referred to Eisberg's Fundamentals of Modern Physics where the matter is thoroughly laid out³. This paper will instead concentrate on those highlights that are relevant to the Ramsauer effect.

In general, solutions to the time independent Schrödinger equation are of the form $\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$, when the potential energy field is spherically symmetric. In this case, there is no ϕ dependence so $\Phi(\phi) = 1$. Another way of stating this is to specify that the quantum number $m = 0$, thus $\Phi_0(\phi) = e^{i0\phi} = 1$. The $\Theta_{l,m}(\theta)$ term is the recognizable Associated Legendre Functions, but in this case, since there is no ϕ dependence, the Associated Legendre Functions reduce to the Legendre Polynomials ($\Theta_{l,0}(\theta) = P_l(\cos \theta)$). Finally, since the electrons in this case are not bound, no quantum number n arises. Thus the radial solutions are spherical Bessel functions and are written $j_l(Kr)$. Thus we can write $j_l(Kr)P_l(\cos \theta)$ as one solution describing a free particle having an orbital angular momentum of $[l(l+1)]^{1/2} \cdot \hbar$. Thus, the first term in equation (1), the term describing the incident flux of electrons, can be written as a sum of these solutions, with each term weighted by a factor a_l . Solving for a_l yields

$$e^{iKr \cos \theta} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(Kr) P_l(\cos \theta) \quad (6)$$

with the factor $(2l+1)i^l = a_l$. These are the partial waves which are incident upon the scattering potential. The total plane wave has a linear momentum of $K\hbar$, and it is comprised of this set of partial waves, each of which has an orbital angular momentum of $[l(l+1)]^{1/2} \cdot \hbar$, an amplitude of $2l+1$, and a phase factor of i^l .

Figure 4 depicts the first four spherical bessel functions which describe the radial dependence of the incident electron flux. Figure 5 depicts the first four legendre polynomials. It doesn't show up in the graph, but $P_0(\cos \theta) = 1$ for all values of $\cos \theta$. Assume that the incident plane wave has a linear momentum such that $K = R^{-1}$ where R is the radius of the spherically symmetric scattering potential. This implies that the product $KR = 1$. Now refer to figure 4. There is a significant probability that the $l = 0$ partial wave component of the plane wave is going to interact with the scattering potential, but there is only the most infinitesimal

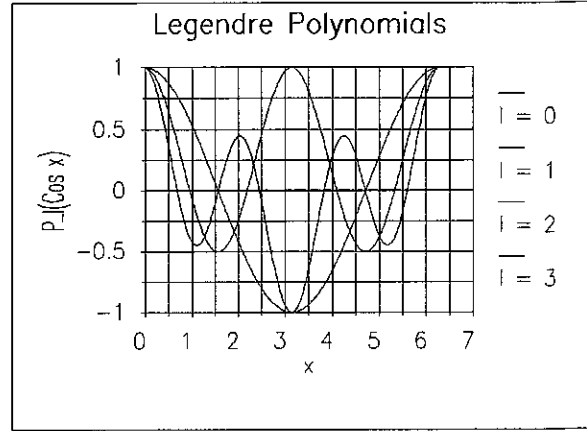
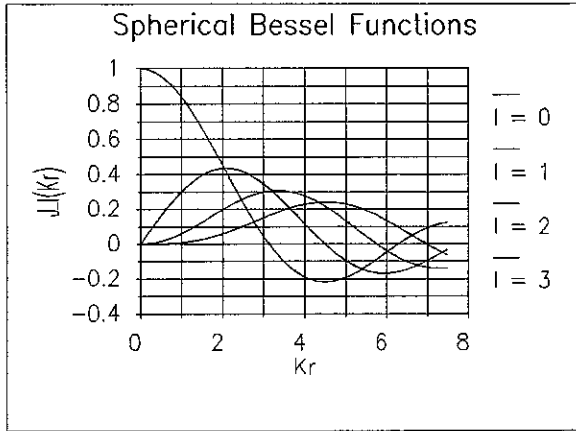


Figure 4: First four spherical Bessel functions.

Figure 5: First four Legendre polynomials.

probability that the $l = 3$ component will interact with the scattering potential. Stated differently, That part of the plane wave which has an orbital angular momentum of \hbar will almost certainly interact with the scattering potential, but the parts of the plane wave with orbital angular momentum of $\sqrt{12}\hbar$ or greater will almost certainly not. The information depicted in figure 5 dictates that in such an event, the $l = 0$ component of the incident wave will scatter isotropically, while any of the $l = 1$ wave which does scatter will scatter principally through angles of 0 and 2π . The main point to be made here is that the product KR defines an upper limit of the components of the plane wave which can interact with the scattering potential.

Regarding Ramsauer's experiment, the electron flux was incident on noble gas atoms. These are closed shell systems which can be approximated nicely by a spherical potential of some effective radius R . Now suppose that the linear momentum of the incident electrons is such that $KR \ll 1$. Figure 4 reveals that all of the scattering will be essentially of the $l = 0$ component. This is an important point in understanding the Ramsauer effect, that it involves scattering principally the $l = 0$ component of the total incident plane wave.

To conclude this analysis of the Ramsauer effect, it is necessary to calculate σ , and that requires an expression of $f(\theta)$ (see equation (5)). Deriving equation (6) to describe the incident flux involved only the first term of equation (1) but the scattered flux involves both terms. The plane waves which emanate from the region of the scattering potential are part of the scattered flux. The general form of the scattered solution will be the same as for the incident plane waves. Furthermore the angular dependence remains unchanged since the angular part of the separated Schrodinger equation doesn't involve the potential energy. But the radial dependence and the coefficients must change. The spherical Bessel functions were solutions for the incident flux because it experienced no potential. The scattered flux solution must reflect the inclusion of a non-zero $V(r)$ term in the radial part of the separated Schrodinger equation. Thus the general form of the scattered solution will be

$$\Psi(r, \theta) = \sum_{l=0}^{\infty} b_l R_l(Kr) P_l(\cos\theta) \quad (7)$$

Eisberg proceeds by making use of the fact that $R_l(Kr)$ is significantly different from $j_l(Kr)$ only in the region of the scattering potential. In the asymptotic regime, the two functions differ by only a phase factor δ_l . In the asymptotic limit

$$j_l(Kr) = \frac{\text{Sin}\left(Kr - \frac{l\pi}{2}\right)}{Kr} ; \quad R_l(Kr) = \frac{\text{Sin}\left(Kr - \frac{l\pi}{2} + \delta_l\right)}{Kr} \quad | \quad r \rightarrow \infty \quad (8)$$

By equating the right side of equation (1) with equation (7), making the appropriate substitutions and solving one finds that $b_l = (2l + 1)i^l e^{i\delta_l}$, and that

$$f(\theta) = \frac{1}{K} \sum_{l=0}^{\infty} (2l + 1) e^{i\delta_l} \text{Sin} \delta_l P_l(\text{Cos} \theta) \quad (9)$$

which in turn yields

$$\sigma = \frac{4\pi}{K^2} \sum_{l=0}^{\infty} (2l + 1) \text{Sin}^2 \delta_l \quad (10)$$

Thus, all that remains is to find the phase shift of $R_l(Kr)$ relative to $j_l(Kr)$. This must be done for each partial wave which is involved in the scattering (as determined by the limiting factor KR). Finding $R_l(Kr)$ involves solving the radial part of the separated Schrodinger equation for the particular scattering potential of interest and subject to the necessary boundary conditions. At this point it is convenient to make a notation change simply to avoid potential confusion. Since R is the effective radius of the scattering potential, and since it is easily confused with $R_l(Kr)$, the function which is a solution to the radial part of the Schrodinger equation will be written $u_l(Kr)$. The effective radius of the scattering potential is still R .

Applying these results to the Ramsauer experiment immediately does away every term in both sums except the $l = 0$ terms, and equations (9) and (10) can be rewritten as

$$f(\theta) = \frac{e^{i\delta_0} \text{Sin} \delta_0}{K} \quad | \quad KR \ll 1 \quad (11)$$

and

$$\sigma = \frac{4\pi \text{Sin}^2 \delta_0}{K^2} \quad | \quad KR \ll 1 \quad (12)$$

Now assume that

$$V(r) = \begin{cases} -V_0 & | \quad r \leq R \\ 0 & | \quad r > R \end{cases} \quad (13)$$

u_0 must satisfy the differential equation

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2} [E - V(r)]u = 0 \quad (14)$$

at every r . In the region $r \leq R$ one can define $K_0 = [2\mu(E + V_0)]^{1/2}/\hbar$ and equation (14) becomes

$$\frac{d^2u}{dr^2} + K_0^2 u = 0 \quad (15)$$

Which is well known to have the general solution $A \cdot \sin(K_0 r) + B \cdot \cos(K_0 r)$. By requiring that $u = 0$ at $r = 0$, the coefficient $B = 0$. Similarly in the region $r > R$ the definition $K = [2\mu E]^{1/2}/\hbar$ results in a differential equation similar to equation (15) and having solutions

$$u = C \sin(Kr) + D \cos(Kr) \quad | \quad r > R \quad (16)$$

Since the objective of this exercise is to find a phase shift δ_0 at $r \rightarrow \infty$, make the following substitutions. Define $C = F \cdot \cos(\delta_0)$ and $D = F \cdot \sin(\delta_0)$. This results in

$$u = F \cos(\delta_0) \sin(Kr) + F \sin(\delta_0) \cos(Kr) = F \sin(Kr + \delta_0) \quad | \quad r > R \quad (17)$$

By imposing the standard constraints of continuity for both u and du/dr at the $r = R$ boundary one finds that

$$\delta_0 = \tan^{-1} \left[\frac{K}{K_0} \tan K_0 R \right] - KR \quad (18)$$

At this point it is illustrative regarding the Ramsauer effect to use a few more assumptions and small angle approximations. It is already known that $KR \ll 1$. Assume also that $K/K_0 \ll 1$ and that $\tan(K_0 R) \gg 1$. Then it is possible to assume that

$$\sin(\delta_0) \approx KR \left[\frac{\tan(K_0 R)}{K_0 R} - 1 \right] \quad (19)$$

which, when substituted into equation (12) yields

$$\sigma \approx 4\pi R^2 \left[\frac{\tan(K_0 R)}{K_0 R} - 1 \right]^2 \quad (20)$$

Conclusion and Discussion

Consider now what happens to σ when the scattered phase shift $\delta_0 = \pi, 2\pi, \dots$. Equation (19) goes to zero, which is to say that $K_0 R$ goes to a value which satisfies the condition $K_0 R = \tan(K_0 R)$. Recall from

the definition of K_0 that this is accomplished by varying the kinetic energy of the scattering electrons. Equation (20) predicts that such a condition will indeed result in a scattering cross section which goes to zero.

Of course, the Ramsauer effect does not result in a scattering cross section of zero, but instead in one which approaches zero. The reason for this is readily seen in figure 4. Even at very small values of Kr , there is a contribution to the scattering from the $l = 1$ partial wave. It would be interesting to test this theory by measuring the angular distribution of the scattered flux that does exist at the Ramsauer minimum. One would expect to find the scattering distributed with maxima at angles of 0 and 2π .

References

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2. E. W. McDaniel, Atomic Collisions, (Wiley, New York, 1989), p. 183.
3. R. M. Eisberg, Fundamentals of Modern Physics, (Wiley, New York, 1961), pp. 534 - 52.