

The Theory of the Continuous X-ray Spectrum in the Immediate
Vicinity of the Short Wavelength Limit

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Summary

In parts I and II the phenomenology of x-rays, especially that part which concerns the Duane-Hunt limit of the continuous spectrum, is very briefly reviewed, and such results of the quantum theory of radiation as are needed in the sequel are stated or developed.

In part III the effect of the extra-nuclear electrons in the atoms composing the target of an x-ray tube on the distribution of energy in the continuous x-radiation from that tube is calculated, using, of course, numerous approximations. The effect of the extra-nuclear electrons is represented by that of a static distribution of charge around the nucleus. The intensity of the x-rays of a given frequency near the Duane-Hunt limit emitted when a beam of cathode rays strikes an atom is found to depend chiefly on the amplitude of the wave function of the scattered electron in the region near the nucleus. This amplitude, and hence the intensity of the x-rays, is calculated as a function of the frequency of the x-rays with two separate assumptions as to the form of the atomic field. The results of these two calculations are rather similar. The behavior of the intensity as a function of the frequency is very sensitive to the parameters describing the form and size of the atomic field. The intensity per unit frequency range may, depending on the values chosen for the parameters describing the field, rise to a sharp maximum at a frequency very close to the

Duane-Hunt limit, which maximum is interpretable as an effect of resonance of the scattered electron with a virtual S level of the atomic field.

The results of the preceding calculations are compared with the measurements of DuMond and Bollman on the continuous x-rays from a tungsten target. It is possible to account for the knee which these workers found in the isochromat in the immediate vicinity of the threshold with a choice of parameters which does not seem at all unreasonable for the tungsten atom. The well known knee that appears at a hundred volts or more from the threshold is, however, not explained by these calculations. The present calculations also throw no light on the discrepancy which apparently exists between the values of h/e , e/m , e , and the Bohr formula for the Rydberg constant.

Part I Introduction

In the year 1895, professor W. C. Röntgen of Würzburg discovered that a previously unknown radiation capable of exciting fluorescence in certain substances, affecting a photographic plate, and rendering the air through which it passes electrically conductive, is produced whenever a beam of fast cathode rays strikes a material body¹⁾. He called the new radiation X-radiation to emphasize its unknown nature. The X-rays travel in straight lines, are unaffected by electric and magnetic fields, and are capable of penetrating every substance to a measurable degree.

Röntgen at first regarded favorably the hypothesis that X-rays consist of longitudinal waves in the ether; but in 1906, Barkla discovered that the X-rays scattered by a material body are polarized, and their transverse character was thus established. Some attempts were made by Haga, Wind, and others to observe diffraction effects in connection with the passage of X-rays through narrow slits. These attempts met with some success, the results indicating a wavelength of the order of 10^{-8} cm. Since this wavelength is smaller than the distance separating neighboring atoms in crystals, it should be possible to observe diffraction effects accompanying the passage of X-rays through crystals. Laue suggested in 1912 that such effects be sought; and, when they were found that same year by Friedrich and Knipping, he gave a theoretical interpretation of the resulting

diffraction patterns. The Braggs showed how crystal diffraction could be used for the accurate measurement of X-ray wavelengths, and the science of X-ray spectroscopy was born.

The spectrum of the X-rays produced by the incidence of a beam of cathode rays on a material target is found to consist of a number of distinct lines whose wavelengths are characteristic of the material of the target, superimposed on a continuous background. The line spectrum, at least in its general structure and most of its details, is interpretable in terms of the Bohr theory of atomic structure, and will not concern us further here. When X-rays were discovered, it was already recognized that cathode rays consist of moving particles bearing an electric charge. According to classical electrodynamics, whenever for any reason an electrified particle is accelerated it must radiate energy in the form of electromagnetic waves. Since X-radiation is produced by the incidence of cathode ray particles on a material target, it was natural to suppose it to be the electromagnetic radiation resulting from the deceleration of these particles by the target. Such an explanation of the origin of X-rays was offered as early as 1896 by Wiechert and a few years later by Stokes and J.J. Thomson. It will not suffice, of course, for the explanation of the line spectrum; but that the X-rays in the continuous spectrum are electromagnetic waves produced by the deceleration of the incident cathode ray particles is today about as

certain as anything ever is. For this reason the continuous X-radiation has come to be called Bremsstrahlung.

In 1915, Duane and Hunt²⁾ published the results of some measurements of the distribution of energy in the continuous X-ray spectrum as a function of the wavelength and of the potential on the X-ray tube. They found that for a fixed potential on the tube no radiation of wavelength less than a well defined minimum, λ_0 , is produced. For wavelengths greater than λ_0 , the intensity of the radiation increases rapidly with the wavelength, reaches a maximum for some intermediate value, and falls less rapidly toward zero as the wavelength is still further increased. Moreover, they found that the limiting wavelength itself depends on the potential on the X-ray tube, being inversely proportional to it. Indeed, they found that if V represent the potential on the X-ray tube, e the charge on the electron, and ν the frequency corresponding to the limiting wavelength λ_0 , the equation

$$(1) \quad eV = h\nu$$

holds, where h is a constant which is equal, within the limits of experimental error, to Plank's quantum of action. These results cannot be explained by any classical theory of Bremsstrahlung, for such a theory would require radiation of all wavelengths to be present, with the intensity falling continuously toward zero as the wavelength decreases; but they are interpretable on the basis of the quantum theory, and are obviously very important for its development.

Equation (1), except for the absence of the work function which is too small to be observable at the potentials used anyway, is identical with Einstein's photoelectric equation which describes the reverse process, namely the ejection of electrons from material bodies by the action of radiation . Just as the validity of Einstein's equation shows the quantum nature of the process of the absorption of radiation, so equation (1) shows the quantum nature of the process of its emission.

On the basis of the quantum theory, the production of radiation by an electron is to be understood as follows: The electron can move without radiating in certain of the classical orbits for the field in which it happens to be (in the case of the production of Bremsstrahlung, this field is that produced by the atoms composing the target). The classical motions characterized by a negative total energy are treated as conditioned periodic and are subjected to the Bohr-Sommerfeld quantum conditions according to which only those motions are possible for which the action variables are integral multiples of Plank's quantum of action, h . The motions with positive energy are not periodic, and all of the classical motions are possible. But while the electron can move in a classical orbit of energy E without radiating, thus violating the laws of classical electrodynamics, there is, however, a certain probability that it will suddenly cease to move in this way and begin moving in another classical orbit of energy E' , at the same time radiating the excess energy as a photon of frequency $\frac{E - E'}{h}$. Such

transitions between states of negative energy give rise to line spectra, while those between states of positive energy give rise to continuous spectra. On this basis equation (1) is immediately understandable. The incident electron has the energy eV , and as there is no classical orbit of negative energy available in the electrically neutral target, it cannot undergo a transition to a state of less energy than zero. Thus, the maximum energy available for radiation is eV , and the maximum frequency possible for the resulting radiation is $\frac{eV}{h}$.

The old quantum theory gave definite, if not always correct, values for the energies of the allowed states of motion and thus for the frequencies of the spectral lines; but it contained no principle which would allow the probabilities of transition between the various states of motion, and thus the intensities of the various spectral lines, unambiguously to be calculated. The best that could be done was to apply the correspondence principle of Bohr, according to which the results of quantum theoretical calculations must agree with those of the corresponding classical calculations in the limit of large quantum numbers, that is, when all the action variables involved are large compared with h . A judicious application of the correspondence principle will enable one to calculate the transition probabilities in terms of the values of certain quantities averaged over both the states involved, but it will not tell one how that average is to be taken. The problem of

continuous spectra is entirely one of intensity, and hence the old quantum theory is in principle unable to deal with it. Nevertheless, by making some plausible assumptions one can treat the case of continuous spectra in an approximate way using the correspondence principle. Kramers³⁾ has calculated in this way the spectral distribution of energy in Bremsstrahlung, basing the correspondence theoretical treatment on the classical radiation of an electron scattered by an atomic nucleus. His results are, in the main, in agreement with experiment.

The question of how the averages demanded by the correspondence principle should be taken was answered in a consistent way only through a fundamental and thorough change in the concepts and laws of mechanics which, initiated in 1925 from opposite points of view by Heisenberg and Schrödinger, has been further developed by these and many other authors into the present theory of quantum mechanics. Quantum mechanical calculations of the distribution of energy in Bremsstrahlung have been made by Oppenheimer, Sommerfeld, and others⁴⁾, the basic process being taken, as in the case of Kramers' calculation, as the collision of an electron with an atomic nucleus. The nature of these calculations will be described in more detail in part II; here only the results need to be stated. It was found that the energy per unit frequency range in the radiation resulting from the collision of a beam of electrons of given current and velocity with an atomic nucleus should be

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zero for frequencies above the limit found by Duane and Hunt. As the frequency decreases past the Duane - Hunt limit, the intensity should rise discontinuously to a value roughly inversely proportional to the energy of the incident electrons. As the frequency decreases still further, the intensity should increase, at first very slowly but later more rapidly, until it becomes infinite as the frequency approaches zero. The high intensity at very low frequencies is in definite contradiction with measurements made on X-rays, but the reason for this is easily understood and will be discussed below. For the rest, the theory agrees rather well with experiment.

The present interest in the problem of Bremsstrahlung is due largely to the circumstance discussed in detail by Birge⁵⁾ that certain measurements of fundamental physical constants are not at the same time consistent with each other and with Bohr's theoretical expression for the Rydberg constant in terms of the fundamental constants. As it is very difficult to see how Bohr's expression for the Rydberg constant can be sufficiently in error to account for the discrepancy, one is led to seek its explanation in the interpretation of the experiments themselves. The most accurate of the measurements involved are the measurement of the charge on the electron, e , both directly by the oil drop method and by measuring the grating space of calcite against that of artificially ruled gratings;

the measurement of the ratio of the charge of the electron to its mass, $\frac{e}{m}$, both by spectroscopic and deflection methods; and the measurement of $\frac{h}{e}$ by determining the position of the Duane-Hunt limit in the continuous X-ray spectrum. In making the measurement of $\frac{h}{e}$ by finding the position of the Duane-Hunt limit, one plots the intensity of the X-rays of a given frequency against the potential on the X-ray tube. This curve should intersect the potential axis at the value V which corresponds according to equation (1) to the frequency ν of the X-rays; but in practice it never does, due partly, at least, to the fact that the monochrometer used has only a finite resolving power. One has, therefore, to extrapolate the curve from the region beyond the threshold in such a way as to remove the fillet. It was thought that the discrepancy between the value of $\frac{h}{e}$ found in this way and its value calculated from the Rydberg constant and the other fundamental constants might be due to an incorrect method of making this extrapolation and that a theoretical examination of the process of the emission of Bremsstrahlung might reveal the correct method. Recently, however, Du Mond and Bollman⁶⁾ have published some measurements of this nature in which they used a monochrometer of higher resolving power than has hitherto been used in such work. A glance at their experimental curve makes the hope of explaining the discrepancy as due to the use of an incorrect method of extrapolation seem

rather futile. At the same time, however, their curve exhibits certain unexpected characteristics which demand explanation and which cannot be explained, at least in any very obvious way, by the theory of Oppenheimer, Sommerfeld, et alii.⁴⁾ These characteristics will be discussed in part IV.

The most obvious defect of the theory of Oppenheimer, and Sommerfeld is that they have considered the Bremsstrahlung produced by a beam of electrons incident on an atomic nucleus, whereas in fact the electrons are incident on atoms which have their full quota of extra-nuclear electrons. This defect is not serious in the case of high frequency X-rays which are still not too near the Duane-Hunt limit, for these rays are produced, on a classical picture, by electrons which are highly accelerated; that is, by electrons which penetrate close to the nucleus where the field of the extra-nuclear electrons is unimportant. X-rays of low frequency, however, are produced by weakly accelerated electrons; that is, they are produced at large distances from the nucleus where the field is weak. In the actual atom the field of the nucleus is rendered almost completely ineffective at large distances by the screening effect of the extra nuclear electrons. One should expect, therefore, that much less low frequency radiation should be observed than is predicted by the theory which completely ignores the screening, and the observations do indeed fulfill this

expectation.

Sauter⁷⁾ has made a quantum mechanical calculation of the intensity of the Bremsstrahlung produced by the incidence of a beam of electrons on an atom which has its full quota of electrons, approximately representing the effect of the external electrons by a continuous distribution of charge in a manner to be discussed in detail in part II. His results are in agreement with experiment for radiation of low frequency, giving much less intensity in this region than do the calculations which completely neglect the extra-nuclear electrons. He has, however, used the Born approximation to the wave functions for both the incident and the scattered electrons. His results are, therefore, invalid for frequencies near the Duane-Hunt limit; for in this region the scattered electron is of low energy and the Born approximation to its wave function invalid.

Nedelsky⁸⁾ has also taken screening into account, using a model similar to one of ours and using accurate wave functions. His calculations are chiefly applicable to the case in which the energy of the incident electron as well as that of the scattered one is small. He finds that as the frequency approaches the Duane-Hunt limit, the intensity per unit frequency range of the Bremsstrahlung falls to zero with the square root of the energy of the scattered electron. He finds also that the intensity considered as a function of the frequency shows maxima and minima which

are caused by resonance of the incident and/or the scattered electron with the atomic field.

The purely classical picture of the process of the production of Bremsstrahlung which we have used with success to predict the effect of the atomic electrons on the X-rays of long wavelength cannot be expected to give even a qualitative idea of the intensity of the X-rays in the neighborhood of the Duane-Hunt limit; for the most conspicuous phenomenon here is the very existence of the limit itself, of which the classical picture gives no hint. We must turn to an at least half quantum theoretical description. In this picture the incident electron of high energy suddenly loses some of its energy under the influence of the atomic field with the simultaneous production of a photon. If the photon is to have a frequency near the Duane-Hunt limit, the electron after radiating must have but little energy. Since the frequency of the radiation produced is high, the process must occur in the region of large field near the nucleus where the screening effect is unimportant; but because of the low energy of the scattered electron, its subsequent motion, and hence the probability of the transition producing it, will be strongly affected by the extra-nuclear electrons. Many essentially quantum phenomena may be interpreted on a classical picture supplemented by a non-classical ability of fields of force to reflect particles. In the present case, we may say that the effect of screening

on the number of incident electrons which penetrate to the region of strong field near the nucleus, and hence on the amount of radiation which would be produced on a classical picture, is negligible. But in order for a photon actually to be produced, the electron must escape from the atom. While now classically the electron will escape from the atom if only its energy is positive, on the basis of quantum mechanics it may suffer a reflection from the field surrounding the nucleus and its escape thereby be prevented and the transition producing it rendered impossible. The probability that an electron will be reflected by a field which it can penetrate classically is large only when the energy of the electron is small, and it is very sensitive to the energy of the electron and to the form of the field. One may thus expect the screening effect of the atomic electrons greatly to influence the intensity of Bremsstrahlung in the neighborhood of the short wavelength limit. But the nature of this influence, whether the intensity in the screened case will be larger or smaller than in the unscreened case, cannot be predicted by these simple considerations; for there is reflection from the Coulomb field also in the unscreened case, and whether the effect of the extra-nuclear electrons will be to increase or to decrease this reflection, cannot be determined without closer investigation.

There is another line of reasoning, mentioned by Nedelsky,⁸⁾ which will, however, yield some definite conclusions regarding the intensity of the Bremsstrahlung

very near the limit. The description given above of the results of the calculations based on the unscreened nucleus is incomplete. The incident electron may not only be scattered with diminished but positive energy; it may also be captured in a state of negative energy with the radiation of a photon of frequency higher than that of the Duane-Hunt limit. Since the electron may be captured only in certain discrete states of negative energy, the Bremsstrahlung so produced has a line spectrum. This line spectrum was not mentioned in the previous discussion because its production is impossible in the actual case to which the results were to be applied as an approximation; namely, in the case of the radiation from an atom possessing its full quota of extra nuclear electrons. There is an infinity of these lines, all with frequencies less than some definite value; and they have their accumulation point at the Duane-Hunt limit. If, now, the intensity per unit frequency range in the region of the line spectrum be defined as the average intensity averaged over a frequency range large compared to the separation of adjacent lines, then the intensity of the Bremsstrahlung is a continuous function of the frequency at the Duane-Hunt limit. This continuity of the intensity of the Bremsstrahlung is a general property which holds independently of the particular form of the field which scatters the cathode rays. In case the atomic field falls more rapidly to zero as the distance from the atom is increased than does a Coulomb

field, that is, in case the atom is electrically neutral, there are no states of negative energy, or at most a finite number of them. In that case the intensity of the Bremsstrahlung must fall continuously to zero as the frequency approaches that of the Duane-Hunt limit unless there happens to exist a stationary state of zero energy, in which case the intensity becomes infinite at the limit.

The intensity in the neighborhood of the high frequency limit of the Bremsstrahlung from high energy cathode rays is thus to be expected to depend to a great extent on the motion of the scattered electron in the field of the atom. As the scattered electron has but little energy its motion must be greatly influenced by the presence of the extra-nuclear electrons and resonance effects analogous to those responsible for the Ramsaur effect⁹⁾ should occur.

Part II The Quantum Theory of Bremsstrahlung

Section 1 The Quantum Theory of Radiation

The modern quantum theory of radiation was first formulated by Dirac¹⁰⁾ in 1927. Dirac's radiation theory now forms part of a more general quantum electrodynamics which was initiated by Heisenberg and Pauli¹¹⁾ and developed by these and other authors. Since these theories are well known and many expositions of them are available in the form of reviews and even of textbooks,¹²⁾ they need not be treated in detail here. Such results as bear directly on the problem at hand will merely be stated, and the reader is referred elsewhere for a more extended discussion of them.

Let a material system involving electrified particles be described with the neglect of all radiative effects by the Hamiltonian H_M . Because of the interaction between the material system and the electromagnetic field, H_M does not suffice for a complete description of the behavior of the system. It must be replaced by $H = H_M + H_R + V$, where H_R depends only on the coordinates describing the state of the electromagnetic field, and V depends both on the coordinates of the material system and on those of the electromagnetic field. In the present state of knowledge the problem defined by the complete Hamiltonian H cannot be solved; or to be more exact, it is not possible to formulate it in such a way that it would have a solution. In such cases, however, that the forces due to the reaction of the radiation field

on the material system are small compared to the other forces acting on it, which is the situation in many actual cases, the effect of the interaction term V may satisfactorily be described by the fiction of transitions between "stationary" states.

Let the material system consist of n particles of masses m_t and charges e_t ($t=1, \dots, n$). The Schrödinger equation for the stationary states of the system is

$$(1) \quad H_m \Psi = E \Psi$$

Let this equation have a discrete set of solutions $\Psi_x(x)$ with the corresponding energy eigenvalues E_x , where x stands for a set of discrete quantum numbers specifying the stationary states. The wave functions Ψ_x may be taken as orthogonal and in the present case of a discrete spectrum as normalized so that we have

$$(2a) \quad \int dx \Psi_{x'}^*(x) \Psi_{x''}(x) = \delta_{x'x''}$$

Here x stands for the set of all the coordinates of all the n particles, the $*$ indicates that the complex conjugate quantity is to be taken, and $\delta_{x'x''}$ stands for the product $\delta_{x'_1 x''_1} \delta_{x'_2 x''_2} \dots$ where $\delta_{\alpha' \alpha''}$ is Kronecker's delta defined by

$$(2b) \quad \delta_{\alpha' \alpha''} = \begin{cases} 1 & \text{if } \alpha' = \alpha'' \\ 0 & \text{if } \alpha' \neq \alpha'' \end{cases}$$

Then, provided the wavelength of the radiation is not short compared to the dimensions of the region which contributes sensibly to the matrix integrals (4), the probability per unit time that the system undergoes a

transition from the state δ' to the state δ'' with the emission of a photon of frequency $\nu = \frac{E_{\delta'} - E_{\delta''}}{h}$, where h is Plank's constant, is given by the expression:

$$(3) \quad A_{\delta' \rightarrow \delta''} = \frac{16 \pi^4 \nu^3}{3 h c^3} \left| \sum_{t=1}^n e_t (\delta'' | \vec{X}_t | \delta') \right|^2$$

where c is the velocity of light, \vec{X}_t represents the coordinates (position vector) of the t^{th} particle, and

$$(4) \quad (\delta'' | \vec{X}_t | \delta') = \int dx \psi_{\delta''}^*(x) \vec{X}_t \psi_{\delta'}(x)$$

The case in which the energy spectrum of the material system is continuous rather than discrete, which is the case that interests us here, requires further discussion, because the wave functions can no longer be normalized according to equation (2) since the integral diverges when $\delta' = \delta''$. The normalization to adopt for the wave function representing the initial state will be clear in any specific case. It is the function that actually represents the initial condition of the system. For example, in the calculation of the intensity of Bremsstrahlung it should be so normalized as to represent definite flux of incident electrons. The problem must be so formulated that the energy of the material system is exactly specified in the initial state; there are no other restrictions. The question of what normalization should be adopted for the wave functions representing the final state, and what interpretation should be placed on formula (3) when such normalization is adopted is, however, more involved.

Let the Hamiltonian H_M of the material system have a continuous energy spectrum. Introduce the energy E itself as one of the parameters (quantum numbers) specifying the stationary states of the system; and let certain other continuous parameters $\gamma, (\gamma, \gamma_1, \dots)$, and for completeness certain discrete parameters $\Gamma, (\Gamma_1, \Gamma_2, \dots)$, be required for the complete specification of the stationary states. We have then a set of orthogonal wave functions $\Psi_{E\gamma\Gamma}(x)$ satisfying the Schrödinger equation:

$$(5) \quad H_M \Psi_{E\gamma\Gamma} = E \Psi_{E\gamma\Gamma} .$$

The initial state of the system may be specified by the wave function $\Psi_0(x)$. Ψ_0 must be energy characteristic, and its energy eigenvalue may be denoted by E_0 ; but it need not be characteristic of any of the observables belonging to the remaining quantum numbers γ and Γ .

Now let the Hamiltonian H_M be modified in a way depending continuously on a parameter λ in such a manner that

$$(6) \quad \lim_{\lambda \rightarrow 0} H_M(\lambda) = H_M(0) = H_M$$

and that the Hamiltonian $H_M(\lambda)$ for values of λ other than 0 possesses a discrete spectrum - discrete not only in regard to energy but also in regard to all the observables necessary completely to specify a stationary state. This modification may be thought of as being brought about by enclosing the system in a large sphere which perfectly reflects all of the particles constituting the material system but which has no effect whatever on the radiation field. It may be necessary to add further devices of this

kind to insure the discreteness of the spectrum with respect to other observables than the energy. The reciprocal of the radius of the sphere may serve as the parameter λ . The eigenfunctions of $H_m(\lambda)$ will be denoted by $\Psi_{\lambda E \delta \Gamma}$, where now E and δ as well as Γ assume discrete values only; and they may be normalized in the usual manner:

$$(7) \quad \int dx \Psi_{\lambda E' \delta' \Gamma'}^*(x) \Psi_{\lambda E'' \delta'' \Gamma''}(x) = \delta_{E' E''} \delta_{\delta' \delta''} \delta_{\Gamma' \Gamma''}$$

The wave function Ψ_0 of the initial state will not be an eigenfunction of $H_m(\lambda)$. A new one, $\Psi_{0\lambda}$, must therefore be introduced satisfying

$$(8) \quad H_m(\lambda) \Psi_{0\lambda} = E_{0\lambda} \Psi_{0\lambda}$$

$$(9) \quad \lim_{\lambda \rightarrow 0} \Psi_{0\lambda} = \Psi_0.$$

Then writing

$$(10) \quad (E' \delta' \Gamma' | \vec{X}_i | 0\lambda) = \int dx \Psi_{\lambda E' \delta' \Gamma'}^*(x) \vec{X}_i \Psi_{0\lambda}(x)$$

equation (3) can be applied in the usual way.

Now let $g_\lambda(E, \delta, \Gamma)$ be a continuous function of the continuous variables E and δ such that $g_\lambda(E, \delta, \Gamma) \Delta E' \Delta \delta'$ is approximately the number of stationary states of $H_m(\lambda)$ with $E' < E < E' + \Delta E'$, $\delta' < \delta < \delta' + \Delta \delta'$, $\Gamma = \Gamma'$ provided $\Delta E'$ and $\Delta \delta'$ are so large that this number is not small but still are not too large. g_λ represents a macroscopic density of stationary states. In the nature of things g_λ is incapable of exact definition. But it becomes the more

precisely definable the smaller becomes λ and hence the more dense become the stationary states; and at the same time, $g_\lambda \rightarrow \infty$. Applying now formula (3), we have the result that

$$\frac{16\pi^4\nu^3}{3hc^3} \left| \sum_{\xi=1}^n e_\xi(E'\delta'\Gamma'|\vec{x}_\xi|0\lambda) \right|^2 g_\lambda(E'\delta'\Gamma') \Delta E' \Delta \delta'$$

gives the probability per unit time that the system undergoes a transition from the initial state to some final state characterized by the quantum numbers E'', δ'', Γ' , where $E' < E'' < E' + \Delta E'$, $\delta' < \delta'' < \delta' + \Delta \delta'$, with the emission of a photon of frequency $\frac{E_{0\lambda} - E''}{h}$. The frequency of the photon must then lie between $\nu = \frac{E_{0\lambda} - E' + \Delta E'}{h}$ and $\nu - \Delta \nu$, where $\Delta \nu = \frac{\Delta E'}{h}$. Thus

$$(11) \quad \frac{16\pi^4\nu^3}{3c^3} \left| \sum_{\xi=1}^n e_\xi(E'\delta'\Gamma'|\vec{x}_\xi|0\lambda) \right|^2 g_\lambda(E'\delta'\Gamma') \Delta E' \Delta \delta'$$

is the probability per unit time that the system undergoes a transition from the initial state to a final state characterized by quantum numbers $\Gamma = \Gamma'$, δ within the range $\Delta \delta'$ of δ' , with the emission of a photon of frequency within the range $\Delta \nu$ of ν . Expression (11) is approximate to the extent that g_λ is approximate. One may, however, expect the limiting form of (11) as $\lambda \rightarrow 0$ to give the exact transition probability per unit δ range per unit frequency range.

As $\lambda \rightarrow 0$, $g_\lambda \rightarrow \infty$. But also the final state wave function $\Psi_{\lambda E''\delta''\Gamma'}$ approaches zero because of the normalizing conditions (7) and the fact that the integral $\int |\Psi_{E'\delta'\Gamma'}|^2 d\lambda$ diverges. Hence the matrix integrals $(E'\delta'\Gamma'|\vec{x}_\xi|0\lambda)$ approach zero, and

we may expect expression (11) to remain finite. If we incorporate the density function g_λ directly into the matrix integral, we may conveniently write:

$$(12) \quad \varphi_{\lambda E' \delta' \Gamma'}(x) = \sqrt{g_\lambda(E' \delta' \Gamma')} \psi_{\lambda E' \delta' \Gamma'}(x)$$

$$(13) \quad [E' \delta' \Gamma' | \vec{X}_t | 0\lambda] = \int \varphi_{\lambda E' \delta' \Gamma'}^*(x) \vec{X}_t \psi_{0\lambda}(x) dx$$

Then

$$(14) \quad \frac{16\pi^4 \nu^3}{3c^3} \left| \sum_{t=1}^n e_t [E' \delta' \Gamma' | \vec{X}_t | 0\lambda] \right|^2$$

gives the approximate transition probability per unit time per unit δ range per unit frequency range. Hence if we can, and do, so normalize the eigenfunctions of the original Hamiltonian H_λ that

$$(15) \quad \psi_{E \delta \Gamma}(x) = \lim_{\lambda \rightarrow 0} \varphi_{\lambda E \delta \Gamma}(x)$$

then the expression (3) when multiplied by h will give the exact transition probability.

The mathematical question of the possibility of this kind of normalization, that is of the existence of the limit indicated in (15), is by no means a simple one. The fact is, however, as was shown by Weyl¹³⁾, that this type of normalization is possible, at least in a great many cases.

It is necessary to obtain another form of the normalizing condition (15) so that in a specific case it may be possible properly to normalize the ~~the~~ wave functions without

actually modifying the Hamiltonian and carrying out the above operations. Such a modified form of the normalizing conditions can be derived from the fact that in the limit $\lambda \rightarrow 0$, sums over the discrete parameters E', δ' may be replaced by integrals over the parameters regarded as continuous variables with the help of the density function g_λ according to the scheme:

$$(16) \quad \sum_{E'} \sum_{\delta'} f(E', \delta') \leftrightarrow \int dE' d\delta' f(E', \delta') g_\lambda(E', \delta').$$

Now from equation (7) we have

$$(17) \quad \sum_{E''} \sum_{\delta''} \sum_{\Gamma''} \int dx \Psi_{\lambda E' \delta' \Gamma'}^*(x) \Psi_{\lambda E'' \delta'' \Gamma''}(x) f(E'' \delta'' \Gamma'') = f(E' \delta' \Gamma')$$

for all functions f . We have also from (7) and (12)

$$(18) \quad \int dx \varphi_{\lambda E' \delta' \Gamma'}^*(x) \varphi_{\lambda E'' \delta'' \Gamma''}(x) = \int dx \Psi_{\lambda E' \delta' \Gamma'}^*(x) \Psi_{\lambda E'' \delta'' \Gamma''}(x) g_\lambda(E'' \delta'' \Gamma'').$$

If now we go to the limit $\lambda \rightarrow 0$ in (17), making use of (16), (18) and (15), we obtain

$$(19) \quad \sum_{\Gamma''} \int dx \int dE'' d\delta'' \Psi_{E' \delta' \Gamma'}^*(x) \Psi_{E'' \delta'' \Gamma''}(x) f(E'' \delta'' \Gamma'') = f(E' \delta' \Gamma')$$

Equation (19) serves uniquely to determine the normalization of the wave functions without resort to the Hamiltonian $H_m(\lambda)$, which has served its purpose by showing how formula (3) is to be interpreted when such wave functions are used. Of course the above manipulations do not demonstrate the possibility of normalizing according to (19); they merely suggest this possibility and show how the wave functions

are to be interpreted in case (19) proves possible. The proof of (19) must rest on Weyl's work.¹³⁾ It should be noted that the order of integration in (19) must be that shown and may not be changed, and that the generality of the function f must be suitably restricted.

Equation (19) may be rewritten in the form

$$(20) \quad \int dx \Psi_{E', \delta', r'}^*(x) \Psi_{E'', \delta'', r''}(x) = \delta_{r', r''} \delta(E' - E'') \delta(\delta' - \delta'')$$

where $\delta(\delta' - \delta'')$ stands for the product $\delta(\delta'_1 - \delta''_1) \delta(\delta'_2 - \delta''_2) \dots$, and $\delta(x)$ is Dirac's delta function defined by the conditions

$$(21) \quad \begin{aligned} x \delta(x) &= 0 \\ \int_{-\infty}^{\infty} \delta(x) dx &= 1. \end{aligned}$$

No function satisfying conditions (21) exists¹⁴⁾, and equation (20) can therefore only be regarded as a symbolic way of writing (19). But to refuse, merely because it does not exist, to use the delta function in those places where it shortens the notation or makes the underlying relations easier to grasp would be pedantry.

Part II

Section 2 The Radiative Collision of an Electron with a Heavy Atom

In this section I wish to discuss in a qualitative way the radiative collision of an electron with a heavy atom with the view of ascertaining the nature of the approximation whereby the many body problem is replaced by that of the collision of an electron with a fixed field, and of determining the physical nature if not the order of magnitude of the terms thereby neglected.

Since the atomic nucleus is thousands of times more massive than the electron, its motion may be neglected from the outset. Let the atom have the atomic number Z , and let x_i ($i=1, \dots, Z$) represent all the space and spin coordinates of the i^{th} atomic electron. The expression $\int \dots dx_i$ will always be understood to include a summation over the spin coordinate. The Hamiltonian H_0 of the atom may be written as follows:

$$(1) \quad H_0 = \sum_{i=1}^Z \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j}^Z F(x_i, x_j)$$

where e and m are the charge and mass of the electron, p_i , the momentum of the i^{th} electron, r_i the distance of the i^{th} electron from the nucleus, and $F(x_i, x_j) = F(x_j, x_i)$ the interaction between the i^{th} and j^{th} electrons. F may also involve the momenta of the electrons, but it is given to a high degree of approximation by $\frac{e^2}{r_{ij}}$, with r_{ij} the distance between the

$i^{\pm 4}$ and $j^{\pm 4}$ electrons. Let the stationary states of the atom be represented by the wave functions $\varphi_s(x_1, \dots, x_z)$, satisfying the Schrödinger equation

$$(2) \quad H_0 \varphi_s = E_s \varphi_s$$

and normalized according to the scheme of section 1. S represents the set of quantum numbers necessary to specify the stationary states. They will have a discrete range, representing the atom in its various excited states, and a continuous range representing the ionized atom. The ground state of the atom will be specified by $S = 0$. $\varphi_s(x_1, \dots, x_z)$ is antisymmetrical in each pair of coordinates x_i, x_j , according to Dirac's form of the Pauli exclusion principle.

It is convenient first to discuss the collision with the neglect of radiative effects, since these are to be described by the fiction of transitions between stationary states of the system. Let the incident electron have the coordinates x_0 . The Hamiltonian for the complete system of atom and incident electron will be

$$(3) \quad H = H_0 + \frac{p_0^2}{2m} - \frac{Ze^2}{r_0} + \sum_{i=1}^z F(x_0, x_i)$$

This Hamiltonian is symmetrical in the coordinates of all the $Z+1$ electrons, but for the time being we shall ignore the formal identity of the incident and the atomic electrons. We must now seek a solution $\Psi(x_0; x_1, \dots, x_z)$ of the Schrödinger equation

$$(4) \quad H\Psi = E\Psi$$

which is antisymmetrical in the variables $X_1 \cdots X_z$ but not necessarily in X_0 . Ψ may then be expanded in a series of the eigenfunctions of the atom alone as follows:

$$(5) \quad \Psi(x_0; x_1 \cdots x_z) = \left(\sum_s + \int ds \right) f_s(x_0) \varphi_s(x_1 \cdots x_z)$$

We must demand of Ψ that the expansion coefficients f have the following asymptotic forms:

$$(6) \quad \begin{aligned} f_0(x_0) &= e^{ik_0 z_0} + r_0^{-1} F_0(\theta_0, \varphi_0) e^{ik_0 r_0} \\ f_s(x_0) &= r_0^{-1} F_s(\theta_0, \varphi_0) e^{ik_s r_0} \end{aligned}$$

Here r_0, θ_0, φ_0 are the spherical coordinates of the incident electron, and z_0 its usual Cartesian coordinate. The following relations which express the conservation of energy will hold:

$$(7) \quad \begin{aligned} k_s^2 &= k_0^2 + K_0^2 - K_s^2 \\ K_s^2 &= \frac{2m}{\hbar^2} E_s \end{aligned}$$

\hbar is here as elsewhere Plank's constant divided by 2π .

The various terms in the expansion of Ψ have now the following interpretations:

f_0 : This term represents an incident beam of electrons of energy $\frac{\hbar^2}{2m} k_0^2$ plus a scattered beam of the same energy. It thus represents the elastic scattering.

f_s , S discrete, $k_s^2 > 0$: This term represents the incident as scattered with the atom left in an excited state.

f_s , S discrete, $k_s^2 < 0$: In such terms, if they exist at all, the coefficient $f_s(x_0)$ decreases exponentially as

becomes large. It therefore represents the incident electron as well as all the atomic electrons as permanently in the vicinity of the nucleus - that is, it represents the formation of a negative ion. Anyway there can be no such terms in the case of high energy collisions.

f_s , S continuous, $k_s^2 > 0$: These terms represent the atom as ionized and the incident electron as scattered.

f_s , S continuous, $k_s^2 < 0$: Here again $f_s(x_0)$ decreases exponentially as r_0 increases, but this time the atom is represented as ionized - that is, with one or more of its electrons removed from the vicinity of the nucleus. In these terms are therefore included all the exchange processes in which the incident electron is captured by the atom and one or more of the atomic electrons emitted. As long as we disregard the identity of the incident with the atomic electrons these processes must be regarded as distinct from all the previously considered processes. Actually, however, they are not distinct processes and their probabilities interfere.

In order to deal with the exchange processes, expand the wave function Ψ as follows:

$$(8) \quad \Psi(x_0; x_1 \dots x_z) = \left(\sum_s + \int ds \right) g_s(x_i) \varphi_s(x_1 \dots x_0 \dots x_z)$$

This may be solved for the coefficients g_s :

$$(9) \quad g_s(x_i) = \int \varphi_s^*(x_1 \dots x_0 \dots x_z) \Psi(x_0; x_1 \dots x_z) dx_1 \dots dx_0 \dots dx_z$$

If the variables x_i and x_i are replaced by each other in equation (9) and then x_i and x_0 interchanged in φ_s^* and x_i and x_0 interchanged in Ψ there results, because of the antisymmetry of the wave functions:

$$(10) \quad g_s(x_i) = \int \varphi_s^*(x_0 x_1 \dots x_z) \Psi(x_0; x_1 \dots x_z) dx_0 dx_1 \dots dx_z$$

Thus it is seen that the functional form of g_s does not depend on which of the atomic electrons is given the privileged rôle in the expansion (8). This is as it must be because the atomic electrons are being treated as indistinguishable.

Now presumably¹⁵⁾ $g_s(x_i)$ has the asymptotic form:

$$(11) \quad g_s(x_i) \sim r^{-1} G_s(\theta, \varphi) e^{i k_s r}$$

The interpretation of the various terms in equation (8) can be discussed in the same way as was that of those in equation (5). Until we come to the last group of terms by which the atom is represented as ionized and the "ejected" electron as having negative energy, similar terms represent similar processes with, however, the difference that the terms in equation (8) represent the incident electron as captured by the atom and the i^{th} atomic electron as ejected. The last group of terms, however, represents the i^{th} electron as permanently in the vicinity of the nucleus with one or more of the other atomic electrons and/or the incident electron removed from it. These terms, therefore, contain

the direct scattering and the exchange processes in which other of the atomic electrons than the i^{th} exchange places with the incident electron.

The probability amplitudes representing direct and exchange processes interfere with each other because of the indistinguishability of the electrons. This effect is taken into account by requiring the wave function either to be symmetrical or antisymmetrical in the coordinates of all the particles. The Pauli exclusion principle shows that in the case of electrons, the wave function must be antisymmetrical. Put therefore:

$$(12) \quad \Psi(x_0, x_1, \dots, x_z) = \Psi(x_0; x_1, \dots, x_z) - \sum_{i=1}^z \Psi(x_i; x_1, \dots, x_z)$$

where in the sum x_0 stands in the place previously occupied by x_i . Ψ will be found to be antisymmetrical in all the electrons because of the antisymmetry of Ψ in the atomic electrons. Of course it also satisfies the Schrödinger equation. From (8) we have:

$$(13) \quad \Psi(x_i; x_0, \dots, x_0, \dots, x_z) = \left(\sum_s + \int ds \right) g_s(x_0) \varphi_s(x_1, \dots, x_z)$$

From (5), (13), and (12) there results:

$$(14) \quad \Psi(x_0, \dots, x_z) = \left(\sum_s + \int ds \right) [f_s(x_0) - Z g_s(x_0)] \varphi_s(x_1, \dots, x_z)$$

The various terms in this expansion give the various processes as before but this time including the exchange effect.

In order to calculate the amount of radiation produced in this collision we have according to section 1 to treat the initial and final states separately and to form the sum of $Z+1$ matrix elements of the type of ((4) section 1). The wave functions for the initial and final states may be distinguished by subscripts i and f . Ψ_i and Ψ_f satisfy the Schrödinger equation (4) but with different values of E , and both will have an expansion similar to (14). The expansion coefficients of Ψ_i and Ψ_f will also be distinguished by subscripts i and f . The matrix element for the radiative transition is then:

$$(15) \quad R = \sum_{k=0}^Z \int \Psi_f^* \vec{\chi}_k \Psi_i dx_0 \cdots dx_z$$

Because of the antisymmetry of the Ψ , all the terms in (15) are equal so that we have:

$$(16) \quad R = (Z+1) \int \Psi_f^* \vec{\chi}_0 \Psi_i dx_0 \cdots dx_z$$

Substituting the expanded forms of Ψ_i and Ψ_f in (16) and performing the integration over dx_1, \dots, dx_z , we have:

$$(17) \quad R = (Z+1) \sum_s \int [f_{fs}^*(x_0) - g_{fs}^*(x_0)] \vec{\chi}_0 [f_{is}(x_0) - g_{is}(x_0)] dx_0$$

Now the terms of (17) for which $s \neq 0$ represent in a sense double processes in which the incident electron excites the atom to the s^{th} state and then the atom falls back to the ground state with the emission of a photon and the ejection of an electron. As double processes we may expect them to

contribute but a small part of the total radiation, most of which we may expect to come from the term $S=0$ in (17). Anyway we shall neglect these "double" processes.

To calculate the wave functions f appearing in (17), put (5) in (4), using the form (3) for H . Reduce this by means of (2), multiply by $\varphi_s^*(x_1, \dots, x_z)$ and integrate over dx_1, \dots, dx_z . There results:

$$(18a) \quad \left(\frac{p_0^2}{2m} + V_{ss} + E_s - E \right) f_s = - \sum_{s' \neq s} V_{ss'} f_{s'}$$

where

$$(18b) \quad V_{s's''}(x_0) = \int dx_1, \dots, dx_z \varphi_{s'}^*(x_1, \dots, x_z) \left[-\frac{Ze^2}{r_0} + \sum_{i=1}^Z F(x_0, x_i) \right] \varphi_{s''}(x_1, \dots, x_z).$$

The solution to (18) that we want is one in which f_0 is much larger than the other f_s . Hence if the quantities $V_{s's''}$ for $s' \neq s''$ are sufficiently small, the set f_s defined by $f_s = 0$ for $s \neq 0$, f_0 a solution to:

$$(19) \quad \left(\frac{p_0^2}{2m} + V_{00}(x_0) + E_0 - E \right) f_0 = 0$$

will be an approximation to the desired solution. $V_{00}(x_0)$ merely represents the average potential at the point x_0 due to the atom in its ground state. Thus using this approximate wave function in (17) we have reduced the problem to that of the radiation of an electron moving in the field of the atom.

Part II

Section 3 The Radiative Collision of an Electron with a Spherically Symmetric Field

In this section I propose to show how the energy J_ν of the radiation of frequency ν emitted per unit time per unit frequency range when a beam of electrons of uniform energy E_0 and constant current is incident on a fixed field in which the electron has the potential energy $V(r)$ has been calculated. Here r is the distance of the electron from a fixed point in the field.

Schrödinger's equation for the electron in this field is:

$$(1) \quad \left(\frac{P^2}{2m} + V - E \right) \Psi = 0$$

The momentum of the electron, \vec{P} , is here to be regarded as the operator $\frac{\hbar}{i} \text{grad}$.

In accordance with section 1 we have to find a solution Ψ_0 to equation (1) for the eigenvalue E_0 representing an incident beam of electrons of unit current plus a scattered wave, and a complete orthogonal set $\Psi_{w\delta}$ of solutions for the eigenvalue E . The wave functions $\Psi_{w\delta}$ are to be normalized according to the scheme:

$$(2) \quad \int \Psi_{w'\delta'}^*(x) \Psi_{w''\delta''}(x) dx = \delta(w' - w'') \delta(\delta' - \delta'')$$

$\delta(\delta' - \delta'')$ must stand for Dirac's or Kronecker's delta according to whether the δ are continuous or discrete valued parameters. The result then is:

$$(3) \quad J_{\nu} = \frac{16\pi^4 h \nu^4 e^2}{3c^3} \sum_{\gamma} |(E\gamma|\vec{x}|0)|^2$$

with

$$(4) \quad (E\gamma|\vec{x}|0) = \int \Psi_{E\gamma}^*(x) \vec{x} \Psi_0(x) d\vec{x}$$

and

$$(5) \quad \nu = \frac{E_0 - E}{h}$$

(3) is obtained from ((14), section 1) by multiplying by $h\nu$ to change from number of photons to energy. \vec{x} is the vector whose rectangular components are the coordinates, x , y , z , of the electron, and $d\vec{x}$ stands for $dx dy dz$.

If we let \vec{v} denote the velocity and \vec{a} the acceleration of the electron we may expect to be able to apply the general formula for the quantum mechanical matrix of the time derivative of a quantity,

$$(6) \quad \left(\frac{dF}{dt}\right)_{n'm''} = \frac{i}{\hbar} (E_{n'} - E_{m''}) F_{n'm''}$$

twice, obtaining

$$(7) \quad (E'\gamma'|\vec{a}|0) = -4\pi^2 \nu^2 (E'\gamma'|\vec{x}|0)$$

and then making use of the equation of motion

$$(8) \quad m\vec{a} = -g\vec{\text{grad}} V$$

to rewrite (3) as follows:

$$(9) \quad J_V = \frac{he^2}{3c^3m^2} \sum_{\gamma} |(E\gamma | (g\vec{r}ad V) | 0)|^2$$

In order to establish the validity of this transformation in the present case, note that with the operator representation of \vec{p} by $\frac{\hbar}{i}g\vec{r}ad$ we have

$$(10) \quad (g\vec{r}ad V) = \frac{i}{\hbar} (\vec{p}V - V\vec{p}) = \frac{i}{\hbar} (\vec{p}H - H\vec{p})$$

where H is the Hamiltonian

$$(11) \quad H = \frac{p^2}{2m} + V$$

The right side of (10) contains two terms and the left side only one because $(g\vec{r}ad V)$ is regarded as the operator "multiply by the gradient of V ," whereas $\frac{i}{\hbar}\vec{p}V$ is the operator "multiply by V and then take the gradient of the resulting expression." Then from (10) we have:

$$(12) \quad (E''\gamma'' | (g\vec{r}ad V) | E'\gamma') = \frac{i}{\hbar} [(E''\gamma'' | \vec{p}H | E'\gamma') - (E''\gamma'' | H\vec{p} | E'\gamma')]$$

Now

$$(E''\gamma'' | \vec{p}H | E'\gamma') = \int d\vec{x} \Psi_{E''\gamma''}^* \vec{p}H \Psi_{E'\gamma'} = E' \int d\vec{x} \Psi_{E''\gamma''}^* \vec{p} \Psi_{E'\gamma'}$$

and because of the fact that H is self adjoint

$$\begin{aligned} (E''\gamma'' | H\vec{p} | E'\gamma') &= \int d\vec{x} \Psi_{E''\gamma''}^* H \vec{p} \Psi_{E'\gamma'} \\ &= \int d\vec{x} H \Psi_{E''\gamma''}^* \vec{p} \Psi_{E'\gamma'} \\ &= E'' \int d\vec{x} \Psi_{E''\gamma''}^* \vec{p} \Psi_{E'\gamma'} \end{aligned}$$

whence the expected formula

$$(13) \quad (E''\delta'' | \text{grad} V | E'\delta') = \frac{i}{\hbar} (E' - E'') (E''\delta'' | \vec{P} | E'\delta')$$

follows. To transform from the \vec{P} to the \vec{x} matrix, note that we have:

$$P_x x - x P_x = \frac{\hbar}{i}$$

whence

$$P_x^2 x - P_x x P_x = \frac{\hbar}{i} P_x$$

$$P_x x P_x - x P_x^2 = \frac{\hbar}{i} P_x$$

and therefore

$$(14) \quad P_x = \frac{i}{2\hbar} (P_x^2 x - x P_x^2) = \frac{im}{\hbar} (Hx - xH),$$

analogous equations holding also for P_y and P_z . In exactly the same manner that (13) was derived from (12),

$$(15) \quad (E''\delta'' | \vec{P} | E'\delta') = -\frac{im}{\hbar} (E' - E'') (E''\delta'' | \vec{x} | E'\delta')$$

may be derived from (14). Then from (3), (5), (13), and (15), (9) follows.

The Schrödinger equation (1) may be written as follows:

$$(16) \quad \nabla^2 \psi + (k^2 - v) \psi = 0$$

with

$$(16a) \quad k^2 = \frac{2m}{\hbar^2} E, \quad v = \frac{2m}{\hbar^2} V.$$

∇^2 is the Laplacian operator. In case v depends on r only, this equation is separable in spherical coordinates¹⁶⁾, and a complete set of single valued solutions is given by:

$$(17) \quad R_{k\ell}(r) P_{\ell}^{|m|}(\cos\theta) e^{im\varphi}$$

where $R_{k\ell}$ satisfies the differential equation:

$$(18) \quad \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(k^2 - v - \frac{\ell(\ell+1)}{r^2} \right) R = 0$$

Here ℓ is any non-negative integer, m any integer such that $|m| \leq \ell$, and $P_{\ell}^{|m|}$ the associated Legendre function.¹⁷⁾ Functions (17) are characteristic besides of the energy, of the total angular momentum and its z component, whose values are $\ell\hbar$ and $m\hbar$ respectively. r, θ, φ are spherical coordinates so chosen that $z = r \cos \theta$.

The angular part of (17) may be normalized by multiplying it by a suitable constant $A_{\ell m}$, so that

$$(19) \quad |A_{\ell m}|^2 \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta P_{\ell}^{|m|}(\cos\theta) e^{-im'\varphi} P_{\ell}^{|m|}(\cos\theta) e^{im''\varphi} = \delta_{\ell'\ell} \delta_{m'm''}$$

The value of $A_{\ell m}$ then is given by:¹⁷⁾

$$(20) \quad |A_{\ell m}|^2 = \frac{2\ell+1}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}$$

If $V(r)$ approaches zero as r increases faster than does $\frac{1}{r}$, then the solution to (18) which is finite at $r=0$ will have the asymptotic form:

$$R_{k\ell} \sim \text{constant} \cdot \sin\left(kr - \frac{\ell\pi}{2} + \eta_{\ell}\right)$$

where η_{ℓ} depends on k and ℓ but not on r . For definiteness let $R_{k\ell}^{(r)}$ be that solution to (18) which is finite at the origin and for which:

$$(21) \quad R_{k\ell}(r) \sim (kr)^{-1} \sin(kr - \frac{\ell\pi}{2} + \eta_\ell)$$

In accordance with the normalizing scheme of section 1 for the wave functions representing the final states of the electron, it is necessary to find a constant $B_{k\ell}$ such that

$$(22) \quad |B_{k'\ell}|^2 \int_0^\infty r^2 dr R_{k'\ell}(r) R_{k''\ell}(r) = \delta(E' - E'')$$

This normalizing constant, once it is admitted that it exists, can be calculated in a manner given by Sommerfeld¹⁹⁾ and ascribed by him to Fues from the asymptotic form alone of $R_{k\ell}$. The fact that only the asymptotic form of $R_{k\ell}$ need be used in this calculation is not surprising, for the delta "function" is singular, and any singular contribution to the integral in (22) must come from the infinite part of the range of integration. According to equation (19) of section 1, equation (22) means

$$(23) \quad |B_{k'\ell}|^2 \int_0^\infty r^2 dr R_{k'\ell}(r) \int_0^\infty dE'' R_{k''\ell}(r) f(E'') = f(E')$$

In (23) write

$$f(E) = \begin{cases} 1 & \text{if } E_1 < E < E_2 \\ 0 & \text{otherwise} \end{cases}$$

and replace dE'' according to (16a) by its equivalent $\frac{\hbar^2}{m} k'' dk''$.

There results:

$$(24) \quad |B_{k'\ell}|^2 \frac{\hbar^2}{m} \int_0^\infty r^2 dr R_{k'\ell}(r) \int_{k_1}^{k_2} k'' dk'' R_{k''\ell}(r) = \begin{cases} 1 & \text{if } k_1 < k' < k_2 \\ 0 & \text{otherwise} \end{cases}$$

The order of integration in (24) may not be changed, but the

expression may be replaced by:

$$(25) \quad |B_{k'l}|^2 \frac{\hbar^2}{m} \lim_{r_0 \rightarrow \infty} \int_{k_1}^{k_2} k'' dk'' \int_0^{r_0} r^2 dr R_{k'l} R_{k''l} = \begin{cases} 1 & \text{if } k_1 < k' < k_2 \\ 0 & \text{otherwise} \end{cases}$$

where now the order of integration is arbitrary. Now from equation (18) written with the parameter k' and multiplied by $R_{k''l}$ subtract the same equation written with k'' and multiplied by $R_{k'l}$. Dropping the subscript l which is understood to appear in the appropriate places, there results:

$$\frac{1}{r^2} [R_{k''} \frac{d}{dr} (r^2 \frac{dR_{k'}}{dr}) - R_{k'} \frac{d}{dr} (r^2 \frac{dR_{k''}}{dr})] + (k'^2 - k''^2) R_{k'} R_{k''} = 0$$

Multiply this equation by $r^2 dr$, integrate from 0 to r_0 , and transpose one term. There results:

$$(26) \quad (k'^2 - k''^2) \int_0^{r_0} r^2 dr R_{k'} R_{k''} = r_0^2 [R_{k'} \frac{dR_{k''}}{dr} - R_{k''} \frac{dR_{k'}}{dr}]_{r=r_0}$$

From (21) we have:

$$R_k(r) = \frac{1}{kr} \sin(kr - \frac{\pi}{2} + \eta) [1 + O(\frac{1}{r})]$$

$$\frac{dR_k(r)}{dr} = \frac{1}{r} \cos(kr - \frac{\pi}{2} + \eta) [1 + O(\frac{1}{r})]$$

If these values be substituted in (26), the result transformed by means of the identity

$$\frac{1}{a} \sin \alpha \cos \beta - \frac{1}{b} \sin \beta \cos \alpha = \frac{1}{2ab} [-(a-b) \sin(\alpha + \beta) + (a+b) \sin(\alpha - \beta)]$$

and the equation divided by $k'^2 - k''^2 = (k' - k'')(k' + k'')$, multiplied by $|B_{k'l}|^2 \frac{\hbar^2}{m} k'' dk''$ and integrated from 0 to r_0 , there results on comparison with (25):

$$(27) \quad \frac{\hbar^2}{2mk'} |B_{k'l}|^2 \lim_{r_0 \rightarrow \infty} \int_{k_1}^{k_2} dk'' \left[\frac{\sin p}{k'' - k'} - \frac{\sin q}{k'' + k'} + O(\frac{1}{r_0}) \right] = \begin{cases} 1 & \text{if } k_1 < k' < k_2 \\ 0 & \text{otherwise} \end{cases}$$

where

$$(27a) \quad \begin{aligned} \rho &= (k'' - k')r_0 + \eta'' - \eta' \\ g &= (k'' + k')r_0 + 2\pi + \eta'' + \eta' \end{aligned}$$

The terms in (27) of the order $\frac{1}{r_0}$ disappear in the limit $r_0 \rightarrow \infty$. If the type of normalization required by section 1 is indeed possible, and we are here assuming that it is, equation (27) must hold for arbitrarily small values of $k_2 - k_1$. But the middle term in (27) is always finite, and hence its integration will yield a term which vanishes with $k_2 - k_1$, and which may therefore be dropped. We are thus left with the first term. Compared with $(k'' - k')r_0$, $\eta'' - \eta'$ is a slowly varying function of k'' if r_0 is sufficiently large. It may then be replaced in the integrand by the value 0 which it assumes when $k'' = k'$, for it is the values of k'' in the neighborhood of k' which contribute most, and in the limit $r_0 \rightarrow \infty$ all, of the value of the integral. We have then:

$$\lim_{r_0 \rightarrow \infty} \int_{k_1}^{k_2} dk'' \frac{\sin \rho}{k'' - k'} = \lim_{r_0 \rightarrow \infty} \int_{k_1}^{k_2} dk'' \frac{\sin(k'' - k')r_0}{k'' - k'} = \lim_{r_0 \rightarrow \infty} \int_{(k_1 - k')r_0}^{(k_2 - k')r_0} \frac{dx}{x} \sin x.$$

In case $k_1 < k' < k_2$, this integral becomes in the limit $\int_{-\infty}^{\infty} \frac{dx}{x} \sin x = \pi$; and if k' does not lie between k_1 and k_2 it becomes indeed zero. Hence from (27) we have

$$(28) \quad |B_{k',l}|^2 = \frac{2m}{\hbar^2} \frac{k'}{\pi}$$

and a set of properly normalized orthogonal wave functions for the specification of the final state of the electron is given by:

$$(29) \quad \Psi_{klm}(r\theta\varphi) = A_{lm} B_k R_{kl}(r) P_l^{lm}(\cos\theta) e^{im\varphi}$$

The wave function Ψ_0 specifying the initial state of the electron must represent for large r a plane incident wave of unit current plus a spherical scattered wave. This function is known to be (20)

$$(30) \quad \Psi_0 = \sqrt{\frac{m}{\hbar k_0}} \sum_{l=0}^{\infty} (2l+1) e^{i(\frac{\pi l}{2} + \eta_l)} R_{k_0 l}(r) P_l(\cos\theta)$$

The matrix element appearing in equation (9) for the intensity is

$$(31) \quad (klm | \vec{g} \text{rad} V | 10) = \int_0^{\infty} r^2 dr \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \Psi_{klm}^* \vec{g} \text{rad} V \Psi_0$$

Now $\vec{g} \text{rad} V = \frac{dV}{dr} \cdot \vec{r}$, where \vec{r} is the unit vector in the r direction - that is, the vector with the rectangular components $\sin\theta \cos\varphi$, $\sin\theta \sin\varphi$, $\cos\theta$. We have now on putting (29) and (30) in (31):

$$(32) \quad (klm | \vec{g} \text{rad} V | 10) = B_k^* A_{lm}^* \sqrt{\frac{m}{\hbar k_0}} \sum_{l_0=0}^{\infty} (2l_0+1) I_{ll_0}(kk_0) (lm | \vec{r} | l_0)$$

where

$$(33) \quad I_{ll_0}(kk_0) = e^{i(\frac{\pi l_0}{2} + \eta_{l_0})} \int_0^{\infty} r^2 dr R_{kl}^*(r) \frac{dV}{dr} R_{k_0 l_0}(r)$$

and

$$(34) \quad (lm | \vec{r} | l_0) = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \cdot P_l^{lm}(\cos\theta) e^{-im\varphi} \vec{r} P_{l_0}(\cos\theta)$$

If the Cartesian components of vector quantities be distin -

guished by a subscript which takes on the values 1, 2, 3, there results:

$$(35) \sum_{l=1}^3 \sum_{l'=0}^{\infty} \sum_{m=-l}^l |(k l m | \text{grad} V | 0)_i|^2 = \frac{m}{\hbar k_0} |\beta_h|^2 \sum_{i=1}^3 \sum_{l'=0}^{\infty} \sum_{m=-l}^l \sum_{l''=0}^{\infty} \sum_{l''=0}^{\infty} (2l'_0+1)(2l''_0+1) \times \\ \times I_{l l'_0} I_{l l''_0}^* |A_{lm}|^2 (l m | \hat{r} | l'_0)_i (l m | \hat{r} | l''_0)_i^*$$

The integrals (34) can be evaluated with the aid of properties of the Legendre functions to be found in reference 17. In accordance with the usual selection rules for optical spectra, they vanish except when $l = l_0 \pm 1$, and $m = \pm 1, 0$. The values of these integrals are:

$$(l m | \hat{r} | l_0)_x = 2\pi (\delta_{m,1} + \delta_{m,-1}) \cdot \frac{l(l+1)}{2l+1} \left\{ \delta_{l_0, l-1} \cdot \frac{1}{2l-1} - \delta_{l_0, l+1} \cdot \frac{1}{2l+3} \right\} \\ (36) \quad (l m | \hat{r} | l_0)_y = \frac{2\pi}{i} (\delta_{m,1} - \delta_{m,-1}) \cdot \frac{l(l+1)}{2l+1} \left\{ \delta_{l_0, l-1} \cdot \frac{1}{2l-1} - \delta_{l_0, l+1} \cdot \frac{1}{2l+3} \right\} \\ (l m | \hat{r} | l_0)_z = 4\pi \delta_{m,0} \cdot \frac{1}{2l+1} \left\{ \delta_{l_0, l-1} \cdot \frac{l}{2l-1} + \delta_{l_0, l+1} \cdot \frac{l+1}{2l+3} \right\}$$

With the values (36) for the integrals involved, the expressions $(l m | \hat{r} | l'_0)_i (l m | \hat{r} | l''_0)_i^*$ can be formed. It should be noted that the cross terms $2\delta_{m,1} \delta_{m,-1}$ appearing in $(\delta_{m,1} \pm \delta_{m,-1})^2$ vanish. These expressions may then be multiplied by $|A_{lm}|^2$ and the summations over m carried out. There results:

$$\sum_m |A_{lm}|^2 (l m | \hat{r} | l'_0)_x (l m | \hat{r} | l''_0)_x^* = 2\pi \cdot \frac{l(l+1)}{2l+1} \left\{ \delta_{l'_0, l-1} \delta_{l''_0, l-1} \cdot \frac{1}{(2l-1)^2} \right. \\ \left. + \delta_{l'_0, l+1} \delta_{l''_0, l+1} \cdot \frac{1}{(2l+3)^2} - (\delta_{l'_0, l-1} \delta_{l''_0, l+1} + \delta_{l'_0, l+1} \delta_{l''_0, l-1}) \cdot \frac{1}{(2l-1)(2l+3)} \right\}$$

$$\sum_m |A_{\ell m}|^2 (\ell m | \vec{r} | l_0')_y (\ell m | \vec{r} | l_0'')_y^* = 2\pi \frac{\ell(\ell+1)}{2\ell+1} \left\{ \delta_{\ell_0', \ell-1} \delta_{\ell_0'', \ell-1} \cdot \frac{1}{(2\ell-1)^2} \right. \\ \left. + \delta_{\ell_0', \ell+1} \delta_{\ell_0'', \ell+1} \cdot \frac{1}{(2\ell+3)^2} - (\delta_{\ell_0', \ell-1} \delta_{\ell_0'', \ell+1} + \delta_{\ell_0', \ell+1} \delta_{\ell_0'', \ell-1}) \cdot \frac{1}{(2\ell+1)(2\ell+3)} \right\}$$

$$\sum_m |A_{\ell m}|^2 (\ell m | \vec{r} | l_0')_z (\ell m | \vec{r} | l_0'')_z^* = 4\pi \cdot \frac{1}{2\ell+1} \left\{ \delta_{\ell_0', \ell-1} \delta_{\ell_0'', \ell-1} \cdot \frac{\ell^2}{(2\ell-1)^2} \right. \\ \left. + \delta_{\ell_0', \ell+1} \delta_{\ell_0'', \ell+1} \cdot \frac{(\ell+1)^2}{(2\ell+3)^2} + (\delta_{\ell_0', \ell-1} \delta_{\ell_0'', \ell+1} + \delta_{\ell_0', \ell+1} \delta_{\ell_0'', \ell-1}) \cdot \frac{\ell(\ell+1)}{(2\ell+3)(2\ell-1)} \right\}$$

The expressions for the x , y , and z , components may now be added. It will be seen that the cross terms involving the expressions $\delta_{\ell_0', \ell-1} \delta_{\ell_0'', \ell+1} + \delta_{\ell_0', \ell+1} \delta_{\ell_0'', \ell-1}$ cancel out. The rest may be slightly reduced by writing $\delta_{\ell_0', \ell_0''}$ $\delta_{\ell_0', \ell \pm 1}$ in place of $\delta_{\ell_0', \ell \pm 1} \delta_{\ell_0'', \ell \pm 1}$ with the result:

$$(37) \quad \sum_{i=1}^3 \sum_m |A_{\ell m}|^2 (\ell m | \vec{r} | l_0')_i (\ell m | \vec{r} | l_0'')_i^* = 4\pi \delta_{\ell_0', \ell_0''} \left\{ \delta_{\ell_0', \ell-1} \cdot \frac{\ell}{(2\ell-1)^2} + \delta_{\ell_0', \ell+1} \cdot \frac{\ell+1}{(2\ell+3)^2} \right\}$$

(37) may now be substituted in (35) and the summations over ℓ_0' and ℓ_0'' carried out. This gives:

$$(38) \quad \sum_{i=1}^3 \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} |(k \ell m | \text{grad} V | 0)_i|^2 = \frac{4\pi m}{\hbar^2 k_0} |B_k|^2 \sum_{\ell=0}^{\infty} \left\{ \ell |I_{\ell, \ell-1}(k, k_0)|^2 \right. \\ \left. + (\ell+1) |I_{\ell, \ell+1}(k, k_0)|^2 \right\}$$

Substituting (38) in (9) and putting for $|B_k|^2$ its value given by (28), we have:

$$(39) \quad J_V = \frac{g}{3} \cdot \frac{\pi e^2}{\hbar^2 c^3} \cdot \frac{k}{k_0} \sum_{\ell=0}^{\infty} \left\{ \ell |I_{\ell, \ell-1}(k, k_0)|^2 + (\ell+1) |I_{\ell, \ell+1}(k, k_0)|^2 \right\}$$

The problem is thus reduced to the solving of the radial Schrödinger equation (18) and the subsequent evaluation of

those integrals (33) for which l and l' differ by unity.

Equation (39) expresses the total intensity of the radiation of a given frequency as a sum of terms each of which may be regarded as the contribution from a transition to a state of definite angular momentum $l\hbar$ from a state in which the angular momentum differs from $l\hbar$ by the amount \hbar . The usual spectroscopic nomenclature may be employed and we may thus speak of the S to P transition etc. Some very rough idea of the relative importance of the different transitions can be obtained from correspondence considerations. In order to produce radiation of high frequency, the electron must be highly accelerated and hence must pass close to the nucleus. An S electron, having no angular momentum, will indeed pass through the origin; but P, D, ... electrons have angular momenta different from zero and therefore will not do so. Furthermore, the smaller the energy of an electron, the greater obstacle does its angular momentum present to its penetration into the central parts of the field. Hence all the possible transitions except that from the P to the S state should be expected to give but a negligible contribution to the radiation near the Duane - Hunt limit, where the scattered electron has very small energy and the frequency of the radiation is high.

If the potential V may be considered constant for values of r greater than some screening radius a , we may say that the radiation from a transition in which the electron

in either the initial or the final state cannot penetrate into the region $r < a$ will be completely negligible. The classical distance, b , of closest approach to the origin of a P electron (angular momentum \hbar) of energy E is given, provided $b > a$ by

$$(40) \quad b = \frac{\hbar}{\sqrt{2mE}}$$

The electron will just get to the edge of the field if $b = a$, that is, if

$$(41) \quad E = \frac{\hbar^2}{2ma^2}$$

If we substitute the Bohr radius, $\frac{\hbar^2}{me^2}$, for a in (41), the value of E that we obtain is about fifteen electron volts. Thus for radiation whose quantum energy is within fifteen electron volts of the high energy limit the contribution from the S to P transition, and indeed from all transitions other than the P to S, should be completely negligible. In an actual case when the energy of the incident electrons is high, it may be supposed that one must go very much farther from the Duane * Hunt limit before the S to P transition becomes important.

Part III The Effect of Nuclear Screening

Section 1 Model Number 1

In the following let all quantities be measured in the system of atomic units introduced by Hartree.²¹⁾ In this system the unit of length is the radius of the Bohr orbit for the ground state of the hydrogen atom, $a_0 = \frac{\hbar^2}{m e^2}$; the unit of charge is the charge on the electron, e ; and the unit of angular momentum is \hbar . The unit of energy in this system is $\frac{e^2}{a_0} = \frac{m e^4}{\hbar^2}$, the value of which is about 27 electron volts.

With this system of units the Schrödinger equation (18) of part II section 3 is

$$(1a) \quad \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left(2E - 2V - \frac{l(l+1)}{r^2} \right) R = 0$$

where E is the energy of the electron. The substitution

$L = rR$ throws this equation into the simpler form

$$(1b) \quad \frac{d^2L}{dr^2} + \left(2E - 2V - \frac{l(l+1)}{r^2} \right) L = 0$$

In the future, whenever it seems desirable, k will be written for the quantity $\sqrt{2E}$.

The potential $V(r)$ must be chosen in such a way as to represent as closely as practical the average potential due to the nucleus of charge Z and the cloud of electrons about it. For small r this potential must be approximately $-\frac{Z}{r}$, and it must approach zero rather rapidly when r becomes larger than the radius of the atom. Since the

potential does fall off rapidly for increasing r it is at once suggested that the potential be treated as actually zero for r larger than some screening radius a . If this is done, then for $r > a$ the Schrodinger equation (1) becomes

$$(2) \quad \frac{d^2 L}{dr^2} + \left(k^2 - \frac{l(l+1)}{r^2} \right) L = 0$$

which has the solution normalized according to part II section 3 equation (21),

$$(3) \quad L_{kl}(r) = \sqrt{\frac{\pi r}{2k}} \left\{ \sin \eta J_{l+\frac{1}{2}}(kr) + \cos \eta J_{-l-\frac{1}{2}}(kr) \right\}$$

Here η is an arbitrary constant, and J represents the usual Bessel functions.²²⁾

Let now $\mathcal{L}_{kl}(r)$ be a solution of (1b) for $r < a$ which vanishes at $r=0$ and is normalized in a way depending essentially only on its behavior for small r . For example, it may be required that the coefficient of the lowest power of r in the expansion of $\mathcal{L}(r)$ as a power series be unity, or a constant value may be specified for some kind of average of $|\mathcal{L}|$ taken over small values of r . Then the solution of (1b) valid for $r < a$ and normalized according to part II section 3 equation (21) is $B_{kl} \mathcal{L}_{kl}(r)$ where B_{kl} is a constant determined by the equations

$$(4) \quad \begin{aligned} B_{kl} \mathcal{L}_{kl}(a) &= L_{kl}(a) \\ B_{kl} \mathcal{L}'_{kl}(a) &= L'_{kl}(a) \end{aligned}$$

in which the primes indicate differentiation with respect

to r . These equations express the continuity of the wave function and its derivative at $r = a$.

The integrals (33) of part II section 3 which determine the intensity of the radiation now become

$$(5) \quad |I_{\ell\ell_0}(k k_0)| = |B_{k\ell}| \cdot |B_{k_0\ell_0}| \cdot \left| \int_0^a dr \cdot \mathcal{L}_{k\ell}^*(r) \cdot \frac{dV}{dr} \cdot \mathcal{L}_{k_0\ell_0}(r) \right|$$

The variation of the intensity of the radiation with frequency is due to the variation of I with k ; and this may itself be regarded as made up of two parts: the variation of the integral itself appearing in (5), and the variation of $B_{k\ell}$. Now in the neighborhood of the Duane - Hunt limit it is this second part, namely, the variation of $B_{k\ell}$, which is of decisive importance. For in this region J_ν must vary rapidly with the frequency ν since it must change from a finite value for ν less than the limiting value ν_0 to zero for ν larger than ν_0 . Equation (1) with $r < a$ does not exhibit any peculiarity for the value zero of k which might account for this behavior of J_ν , for the potential V may, and in general will, contain a constant term, say C ; and any such peculiar behavior of the wave function \mathcal{L} would occur, if at all, for the value $-C$ rather than zero of k . The value of $B_{k\ell}$, however, depends on the solution of equation (2); and for this equation the value zero of k is peculiar. Thus, comparing (5) with equation (39) of part II section 3 and neglecting all transitions except that from the P to the S state, we can say that for frequencies

sufficiently near the Duane-Hunt limit the intensity of radiation is practically proportional to $k|B_{k0}|^2$.

While it can hardly be doubted that the above approximation is valid for frequencies sufficiently near the Duane-Hunt limit, the question of the range of its validity - of how near is sufficiently near - is not easily settled in a satisfactory manner. The integral in (5) contains in the integrand besides the factor $\frac{dV}{dr}$ the product of two oscillatory functions whose periods and amplitudes vary with r . One of these functions is not affected by changes in k ; the amplitude of the other does not vary greatly with k because of the way in which it is normalized, but its period does. Let $N(k)$ be the number of periods of $\mathcal{L}_{k,r}$ in the range $0 < r < a$. Inasmuch as N is not a small number and the other oscillatory function, \mathcal{L}_{k_0, r_0} , has a still larger number of periods, it may be expected that the integral in question will not change greatly until k changes enough to cause N to change by one unit. The approximation may thus be supposed valid over a range of energies given by $\left(\frac{dE}{dN}\right)_{E=0}$.

One has now approximately

$$N = \int_0^a \frac{dr}{\lambda}$$

where λ is the wave length of an electron of total energy E at the position r . The wavelength of the electron of kinetic energy $E - V$ is given by

$$\lambda = \frac{2\pi}{\sqrt{\lambda(E-V)}}$$

whence

$$\left(\frac{dN}{dE}\right)_{E=0} = \frac{d}{dE} \cdot \frac{1}{\sqrt{2}\pi} \int_0^a \sqrt{E-V} dr \Big|_{E=0} = \frac{1}{\sqrt{2}\pi} \int_0^a \frac{dr}{\sqrt{-V}}$$

If for V is chosen the potential due to a nucleus of atomic number Z screened by Z units of charge spread uniformly over the surface of a sphere of radius a , that is,

$$(6) \quad \begin{aligned} V &= Z \left(\frac{1}{a} - \frac{1}{r} \right) \quad \text{for } r < a \\ V &= 0 \quad \text{for } r > a \end{aligned}$$

there results

$$\left(\frac{dN}{dE}\right)_{E=0} = \frac{1}{\sqrt{2}\pi} \int_0^a \frac{dr}{\sqrt{Z(1/r - 1/a)}} = \frac{1}{4\sqrt{2}} \cdot \frac{a^{3/2}}{Z^{1/2}}$$

The approximation in question may thus be expected to be valid for energies up to the order of $4\sqrt{2} Z^{1/2} a^{-3/2}$. The screening radius will be of the order of unity, so with an atomic number of 50 this will be an energy of about 40 atomic units or 1000 electron volts.

The quantity $B_{k,l}$ may now be calculated from equations (4) using the value (3) for the wave functions for $r > a$. (3) may be rewritten

$$(7) \quad L = \frac{1}{k} \sqrt{\frac{\pi}{2}} \left\{ \sin \eta \sqrt{z} J_{l+\frac{1}{2}}(z) + \cos \eta \sqrt{z} J_{-l-\frac{1}{2}}(z) \right\}$$

with $z = kr$. Using the prime to indicate differentiation with respect to the argument so that $[\sqrt{z} J(z)]' = \frac{d}{dz} [\sqrt{z} J(z)]$, but

$$L' = \frac{dL}{dr}, \quad \text{equations (4) become}$$

$$(8) \quad \begin{aligned} B_{kl} \mathcal{L}_{kl} &= \frac{1}{k} \sqrt{\frac{\pi}{z}} \left\{ \sin \eta \sqrt{z} J_{l+\frac{1}{2}}(z) + \cos \eta \sqrt{z} J_{-l-\frac{1}{2}}(z) \right\} \\ B_{kl} \mathcal{L}'_{kl} &= \sqrt{\frac{\pi}{z}} \left\{ \sin \eta [\sqrt{z} J_{l+\frac{1}{2}}(z)]' + \cos \eta [\sqrt{z} J_{-l-\frac{1}{2}}(z)]' \right\} \end{aligned}$$

Solve these equations for $\sin \eta$ and $\cos \eta$, square and add the results, and solve the resulting equation for B_{kl}^2 .

There results

$$(9) \quad B_{kl}^2 = \frac{\pi}{z} \Delta^2 \left\{ \left| \begin{array}{cc} k \mathcal{L}_{kl} & \sqrt{z} J_{l+\frac{1}{2}}(z) \\ \mathcal{L}'_{kl} & [\sqrt{z} J_{l+\frac{1}{2}}(z)]' \end{array} \right|^2 + \left| \begin{array}{cc} k \mathcal{L}_{kl} & \sqrt{z} J_{-l-\frac{1}{2}}(z) \\ \mathcal{L}'_{kl} & [\sqrt{z} J_{-l-\frac{1}{2}}(z)]' \end{array} \right|^2 \right\}^{-1}$$

with

$$(10) \quad \Delta = \begin{vmatrix} \sqrt{z} J_{l+\frac{1}{2}}(z) & \sqrt{z} J_{-l-\frac{1}{2}}(z) \\ [\sqrt{z} J_{l+\frac{1}{2}}(z)]' & [\sqrt{z} J_{-l-\frac{1}{2}}(z)]' \end{vmatrix}$$

Now

$$(11) \quad \Delta = \sqrt{z} J_N(z) [\sqrt{z} J_{-N}(z)]' - \sqrt{z} J_{-N}(z) [\sqrt{z} J_N(z)]'$$

where N has been written in place of $l+\frac{1}{2}$. Hence

$$(12) \quad \frac{d\Delta}{dz} = \sqrt{z} J_N(z) [\sqrt{z} J_{-N}(z)]'' - \sqrt{z} J_{-N}(z) [\sqrt{z} J_N(z)]''$$

But now $\sqrt{z} J_{\pm N}(z)$ are solutions to the differential equation

$$y'' = Qy \quad \text{where } Q = \frac{N^2 - \frac{1}{4}}{z^2} - 1. \quad (22)$$

Therefore

$$\frac{d\Delta}{dz} = \sqrt{z} J_N(z) \cdot Q \cdot \sqrt{z} J_{-N}(z) - \sqrt{z} J_{-N}(z) \cdot Q \cdot \sqrt{z} J_N(z) = 0$$

and Δ is a constant. Δ may thus be evaluated by using the limiting form of the Bessel functions either for large or for small z . This gives $\Delta = -\frac{z}{\pi} \sin \pi N$ or in our case, with $N = l+\frac{1}{2}$,

$$(13) \quad \Delta = (-1)^{l+1} \cdot \frac{z}{\pi}$$

The case $l=0$ is of special interest. We have ⁽²²⁾

$$(14) \quad \sqrt{\frac{z}{\pi}} J_{\frac{1}{2}}(z) = \sqrt{\frac{z}{\pi}} \sin z, \quad \sqrt{\frac{z}{\pi}} J_{-\frac{1}{2}}(z) = \sqrt{\frac{z}{\pi}} \cos z$$

Putting (13) and (14) in (9) and expanding the determinants, there results

$$(15) \quad B_{k_0}^2 = [k^2 \mathcal{L}_{k_0}^2 + \mathcal{L}'_{k_0}{}^2]^{-1}$$

and the intensity of the radiation, being proportional to $k B_{k_0}^2$, will satisfy

$$(16) \quad J_\nu \propto [k \mathcal{L}_{k_0}^2 + \frac{\mathcal{L}'_{k_0}{}^2}{k}]^{-1}$$

In order to calculate the wave functions appearing in (16) some method of approximation must be adopted. The method devised by Wentzel, Kramers, and Brillouin,²³⁾ (W.K.B. method) at once suggests itself. When considered as applied specifically to Schrödinger's equation, this method consists in expanding the action function in powers of \hbar and retaining only the two lowest order terms. For the differential equation

$$(17) \quad \frac{d^2 \mathcal{U}}{dx^2} + \varphi(x) \mathcal{U} = 0$$

it leads to the approximate solution

$$(18) \quad \mathcal{U}_0 = A \varphi^{-1/4} e^{i \int \sqrt{\varphi} dx} + B \varphi^{-1/4} e^{-i \int \sqrt{\varphi} dx}$$

By differentiating \mathcal{U}_0 , one finds that

$$(19) \quad \frac{d^2 \mathcal{U}_0}{dx^2} + \varphi(x) \mathcal{U}_0 \left[1 + \frac{1}{4} \varphi^{-2} \varphi'' - \frac{5}{16} \varphi^{-3} \varphi'^2 \right] = 0$$

where the primes indicate differentiation with respect to x .

Thus the condition for the validity of this approximation is

$$(20) \quad \left| \frac{4\varphi\varphi'' - 5\varphi'^2}{16\varphi^3} \right| \ll 1.$$

(20) ceases to hold in the neighborhood of any point at which φ vanishes - that is, in case (17) is a Schrödinger equation, at which the kinetic energy vanishes. In case (17) is the equation (1b) in which V represents a Coulomb field, (20) is also violated near $r=0$, even when $\ell=0$.

In case (17) is the Schrödinger equation for a problem in which the kinetic energy is everywhere positive and becomes asymptotically independent of x for x very large and also for x very small, it will be seen that of the two independent approximate wave functions in (18) each represents a beam of particles moving in one direction only. There is thus in the W.K.B. approximation no connection between a beam of particles moving in one direction and a beam of particles moving in the opposite direction. This is merely another way of stating that the effects of the reflection of particles from potential "humps" are neglected in the W.K.B. approximation. Hence in so far as the effect being sought here is describable, as it was described in part I, in terms of the reflection of the scattered electron from the field about the nucleus, the W.K.B. approximation should fail to give it.

That the effect sought here is indeed neglected in the

W.K.B. approximation is best seen by making the calculation, which is very simple. If (17) is regarded as equation (1b) with $\ell=0$, the approximate solution (18), with appropriate choice of the arbitrary constants, may be written

$$(21) \quad \mathcal{L} = \frac{1}{\sqrt{k^2 - 2V}} \sin\left(\int_0^r \sqrt{k^2 - 2V} dr + \delta\right)$$

δ is here an arbitrary constant which is to be so determined that (21) will be an approximation to that solution of (1b) which vanishes when $r=0$. It cannot simply be set equal to zero because near $r=0$ (21) is no longer an approximation to any solution of (1b). (21) as written is normalized in a way consistent with the requirements stated on page 46. For $r > a$, $V=0$, and (21) becomes

$$(22) \quad \mathcal{L} = k^{-1/2} \sin\left(kr - ka + \int_0^a \sqrt{k^2 - 2V} dr + \delta\right)$$

To normalize this in accordance with equation (21) of part II section 3 one must multiply it by $k^{-1/2}$. This gives $B_{k_0} = k^{-1/2}$ and the intensity of radiation, which is proportional to $k B_{k_0}^2$ is constant. This result is independent of the particular form chosen for the potential if only it vanishes for large r .

The region in which the above W.K.B. treatment breaks down most seriously is just inside the screening radius; for φ is small there when r is small but φ' is not zero and for the potential (6) not even small. Kramers²³⁾ and others have devised "connection" formulae" which enable one under

certain circumstances to find what W.K.B. solution is approximate on one side of a point at which φ vanishes to the correct solution of the wave equation to which a given W.K.B. solution is approximate on the other side. With the help of these formulae certain problems involving reflection may be treated. This device, however, cannot be used in the present case because the kinetic energy never vanishes but is positive on both sides of the troublesome region. This difficulty could be avoided by choosing a straight line to represent the potential in the neighborhood of $r = a$: that is, by choosing

$$V = 0 \text{ for } r > a$$

$$V = A(r-a) \text{ for } b < r < a$$

and some approximate form for $r < b$. In the region $b < r < a$ the Schrödinger equation can be solved exactly in terms of Bessel functions of the orders $\pm \frac{1}{3}$. The constants A and b would be so chosen that the W.K.B. approximation would be valid near $r = b$. The arbitrary constants in the exact solution valid for $b < r < a$ would be adjusted by matching its amplitude and phase to those of a W.K.B. solution valid for $r < b$. This could in turn be matched to the exact solution of the wave equation in the form of a power series for small values of r . Thus the wave functions appearing in (16) could be obtained. The matching at $r = b$ is greatly facilitated by the circumstance that the condition for the validity of the W.K.B. approximation at $r = b$ is just the

condition that the Bessel functions appearing in the exact solution for $b < r < a$ may be replaced by the first term of their respective asymptotic expansions.

This somewhat complicated procedure can be considerably simplified by the use of a modified form of the W.K.B. method recently introduced by R. E. Langer.²⁴⁾ Langer's method supplies an approximate solution of the differential equation

$$(23) \quad \frac{d^2 \mathcal{U}}{dx^2} + Q^2(x) \cdot \mathcal{U} = 0$$

which reduces to the W.K.B. solution in any region in which the latter is valid, but which may also be valid in the neighborhood of one zero of Q^2 . If, namely, Q^2 have a zero of order ν at the point $x = x_1$, Langer's approximate solution is

$$(24) \quad \mathcal{U}_0 = Q^{-1/2} \xi^{1/2} \{ A J_{-\mu}(\xi) + B J_{\mu}(\xi) \}$$

where

$$(24a) \quad \mu = \frac{1}{\nu + 2}$$

$$(24b) \quad \xi = \int_{x_1}^x Q dx$$

A and B are arbitrary constants, and $J_{\pm\mu}$ are the Bessel functions of order $\pm\mu$. This approximate solution satisfies the equation

$$(25) \quad \frac{d^2 \mathcal{U}_0}{dx^2} + (1 - \omega) Q^2 \mathcal{U}_0 = 0$$

with

$$(25a) \quad \omega = \frac{3}{4} \frac{Q'^2}{Q^4} - \frac{1}{2} \frac{Q''}{Q^3} - \left(\frac{1}{2} + \mu\right) \left(\frac{1}{2} - \mu\right) \xi^{-2}$$

the primes indicating differentiation with respect to x . The solution (24) is valid on both sides of the zero of Q^2 at x_1 and in the neighborhood of x_1 itself, but it breaks down in the neighborhood of a second zero of Q^2 . Replacing the Bessel functions in (24) by their asymptotic forms reduces Langer's solution to the ordinary W.K.B. solution. Comparison of the asymptotic forms of (24) on the two sides of x_1 yields the usual connection formulae of Kramers.

Langer's solution may be used in place of the W.K.B. solution to represent the wave function in the neighborhood of $r = a$, thus obviating the necessity of replacing the potential in that region by a linear function. In order that this may be done, however, it is necessary that the kinetic energy actually vanish at some point near $r = a$. The vanishing of the kinetic energy can be secured by choosing for the potential some function which vanishes at $r = a$ but which continues to increase with r for $r > a$. In particular the potential (6) may be used, using the same form for $r > a$ as for $r < a$.

The approximate solution (24) is not applicable in the neighborhood of $r = 0$ when the potential represents a Coulomb field, since the difficulty here is not caused by the vanishing of the kinetic energy but by its becoming infinite. Langer has given special attention to this case. As an approximate solution of the equation

$$(26) \quad \frac{d^2 \mathcal{U}}{dr^2} + \left[k^2 + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] \mathcal{U} = 0$$

which vanishes at $r=0$, he finds

$$(27) \quad \mathcal{U}_1 = \left\{ \frac{\int_0^r Q_2 dr}{Q_2} \right\} J_{\lambda, \lambda+1} \left(\int_0^r Q_2 dr \right)$$

in which

$$(27b) \quad Q_2^2 = k^2 + \frac{2Z}{r}$$

The function \mathcal{U}_1 , which is normalized in accordance with the requirements stated on page 46 as it stands, may be taken to represent the solution of equation (1) with potential (6) for small values of r . In case this approximation is not valid for such large values of r as a , and it will not be for small energy, a solution of type (24) may be used to represent the wave function for the larger values of r . The arbitrary constants in this solution may be determined by matching it to (27) at some intermediate value of r at which both solutions are valid.

Equation (1b) with the potential (6) may be written

$$(28) \quad \frac{d^2 L}{dr^2} + \left[-2\epsilon + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] L = 0$$

with

$$(28a) \quad \epsilon = \frac{Z}{a} - E$$

Writing

$$(29a) \quad \mathcal{K} = 2\sqrt{2\epsilon}$$

$$(29b) \quad n = \frac{2Z}{\chi}$$

$$(29c) \quad x = \chi r$$

equation (28) takes the form

$$(30) \quad \frac{d^2 L}{dx^2} + \left[-\frac{1}{4} + \frac{n}{x} - \frac{\rho(\rho+1)}{x^2} \right] L = 0$$

The approximate solution (27) for equation (30) is

$$(31) \quad u_0 = \frac{\sqrt{\Phi}}{\sqrt{\frac{n}{x} - \frac{1}{4}}} J_{2j+1}(\Phi)$$

with

$$(31a) \quad \Phi = \int_0^x \sqrt{\frac{n}{x} - \frac{1}{4}} dx$$

A change of variable from x to \sqrt{x} reduces the integral in (31a) to a standard form, and the result of the integration is

$$(31b) \quad \Phi = 2n \left[z \sqrt{1-z^2} + \sin^{-1} z \right]$$

with

$$(31c) \quad z = \frac{1}{2} \sqrt{\frac{x}{n}}$$

The introduction of $x = \chi r$ in place of r has led to the result that (31) is not normalized in conformity with the conditions stated on page 46. In order properly to normalize it, its approximate value for small r must be calculated.

We have

$$\begin{aligned}\Phi &\approx 4\pi z = 2\sqrt{\pi x} \\ \left[\frac{\pi}{x} - \frac{1}{4}\right]^{-\frac{1}{4}} &\approx \sqrt[4]{\frac{x}{\pi}} \\ J_{2l+1}(\Phi) &\approx \text{const.} \cdot \Phi^{2l+1} \approx \text{const.} \cdot (\pi x)^{l+\frac{1}{2}}\end{aligned}$$

whence

$$u_0 \approx \text{const.} \cdot \sqrt[4]{\pi x} \cdot \sqrt[4]{\frac{x}{\pi}} \cdot (\pi x)^{l+\frac{1}{2}} = \text{const.} \cdot x^{l+1} \pi^{l+\frac{1}{2}}$$

Hence in order to normalize the function properly one must divide it by $x^{l+1} \pi^{l+\frac{1}{2}}$. Accordingly we write

$$(32) \quad u_0 = \frac{A}{x^{l+1} \pi^{l+\frac{1}{2}}} \cdot \Phi^{\frac{1}{2}} \left[\frac{\pi}{x} - \frac{1}{4}\right]^{-\frac{1}{4}} J_{2l+1}(\Phi)$$

where A is a constant, independent of the energy, to be fixed later.

Replacing the Bessel function in (32) by its asymptotic form we have

$$(33) \quad u_0 \sim \frac{A}{x^{l+1} \pi^{l+\frac{1}{2}}} \cdot \sqrt{\frac{2}{\pi}} \cdot \left[\frac{\pi}{x} - \frac{1}{4}\right] \cdot \cos\left[\Phi - \left(l + \frac{3}{4}\right)\pi\right]$$

This is simply a W.K.B. solution for the case $l=0$. The condition for its validity is (20) together with the condition that the centrifugal force term, $\frac{l(l+1)}{x^2}$, be negligible. (20) is in this case

$$(34) \quad 4 \cdot \frac{3\pi^2 - 2\pi x}{x[4\pi - x]^3} \ll 1.$$

Under some circumstances (33) will be a good approximation to the wave function clear out to $r=a$. If the energy of the scattered electron measured in terms of the "screening energy" $\frac{Z}{a}$ be introduced as the parameter \mathcal{E} so that

$$(35a) \quad \mathcal{E} = E \cdot \frac{a}{Z}$$

and if one writes

$$(35b) \quad \sigma = \sqrt{2Za}$$

one obtains from equations (28a) and (29)

$$(35c) \quad \epsilon = \frac{Z}{a} (1 - \mathcal{E}) = \frac{\sigma^2}{2a^2} (1 - \mathcal{E})$$

$$(35d) \quad \chi = \frac{2\sigma}{a} \sqrt{1 - \mathcal{E}}$$

$$(35e) \quad \eta = \frac{\sigma}{2\sqrt{1 - \mathcal{E}}}$$

$$(35f) \quad k = \frac{\sigma}{a} \sqrt{\mathcal{E}}$$

$$(35g) \quad (x)_{r=a} \equiv \chi a = 2\sigma \sqrt{1 - \mathcal{E}}$$

Written in terms of these parameters, the condition that

(33) hold at $r=a$ is

$$(36) \quad \frac{8\mathcal{E} - 5}{16\sigma^2 \mathcal{E}^3} \ll 1$$

or roughly

$$(36a) \quad \sqrt{2} \sigma \mathcal{E} \gg 1$$

If, now, one substitutes χ_l with $l=0$ for \mathcal{L} in (16) there results after some reduction

$$(37) \quad J_\nu \propto \frac{\pi}{2} \cdot \frac{\sigma^2}{a} \cdot \frac{1}{A^2} \cdot \left\{ \cos^2\left(\Phi - \frac{3\pi}{4}\right) + \left[\sin\left(\Phi - \frac{3\pi}{4}\right) - \frac{1}{4\sigma \mathcal{E}^{3/2}} \cos\left(\Phi - \frac{3\pi}{4}\right) \right]^2 \right\}^{-1}$$

Whenever (36a) is satisfied and \mathcal{E} itself is not small so that (36) is also satisfied,

$$\frac{1}{4\sigma \mathcal{E}^{3/2}} \ll 1$$

and the right side of (37) reduces approximately to the

constant $\frac{\pi\sigma^2}{2a} \cdot \frac{1}{A^2}$. Thus, whenever the Langer solution valid near $r=0$ is also valid at $r=a$ it gives a constant value for the intensity. This is what should be expected in view of the fact that the W.K.B. approximation neglects the effects of the reflection of electrons. When \mathcal{E} is large enough to satisfy (36), the other approximations that have been made will in general no longer be valid; therefore (37) can never be expected to give the true course of the intensity. Nevertheless it will be convenient for purposes of comparison so to choose the normalizing constant A in \mathcal{U}_0 that the constant value of the right side of (37) - that is, of (16) - for large \mathcal{E} shall be unity. Accordingly we take

$$(38) \quad A^2 = \frac{\pi\sigma^2}{2a}$$

It is necessary now to find the Langer solution (24) of equation (30). Comparing (23) with (30) we find that in this case

$$(39) \quad Q^2(x) = -\frac{1}{4} + \frac{\pi}{x} - \frac{\ell(\ell+1)}{x^2}$$

Q^2 has simple zeros at the points $x = \lambda(n \pm R)$ where

$$(40) \quad R = +\sqrt{\pi^2 - \ell(\ell+1)}$$

For values of x between these two roots, Q^2 is positive and Q is real. Introducing C and η as arbitrary constants, we can write the approximate solution (24) as follows:

$$(41) \quad u_1 = C Q^{-1/2} \xi^{1/2} \left[\cos\left(\frac{\pi}{3} + \eta\right) J_{1/3}(\xi) + \cos\left(\frac{\pi}{3} - \eta\right) J_{2/3}(\xi) \right]$$

with

$$(41a) \quad \xi = \int_x^{x_0} Q dx$$

where Q is given by (39) and x_0 is the greater of the roots of $Q^2 = 0$:

$$(41b) \quad x_0 = 2(\pi + \theta)$$

ξ has here been given the sign opposite to that which it had in (24b) in order to avoid imaginaries in the arbitrary constants. By replacing the Bessel functions in (41) by their asymptotic forms one easily finds that

$$(42) \quad u_1 \sim C \cdot \frac{\sqrt{3}}{2} \cdot \sqrt{\frac{2}{\pi}} Q^{-1/2} \cos\left(\xi + \eta - \frac{\pi}{4}\right)$$

The constants C and η in (41) are to be determined by comparing (42) with (33) at some value x , of x between zero and πa . If the comparison is made at such a place that the term $\frac{\rho(\rho+1)}{x^2}$ is negligible in Q^2 , and this condition is necessary in any case for the validity of (33) and is satisfied everywhere in the important case $\rho=0$, there results

$$(43a) \quad C = \frac{2A}{\sqrt{3} x^{\rho+1} \pi^{\rho+1/2}}$$

$$(43b) \quad \eta = -\xi_1 - \Phi_1 + (\rho+1)\pi$$

where ξ_1 and Φ_1 are the values of ξ and Φ respectively at

the point $x = x_1$. Differentiation of (43b) with respect to x_1 shows at once that to the extent that $\frac{\ell(\ell+1)}{x^2}$ is negligible in Q , η is independent of the point at which the wave functions are matched. In the important case $\ell=0$, η is accurately independent of x_1 , and one need not trouble himself about the matching point further than to make sure that it exists - that is, that there exists a point at which both (33) and (42) are valid approximations to the wave function. For $\ell=0$ one obtains

$$(43c) \quad c^2 = \frac{2\pi a^2}{3x^2 \pi a}$$

$$(43d) \quad \eta = \pi - \int_0^{x_0} \left[\frac{\pi}{x} - \frac{1}{4} \right]^{1/2} dx = -\pi(\pi-1)$$

$$(44) \quad \mathfrak{f} = -2\pi \left[\mathfrak{z} \sqrt{1-\mathfrak{z}^2} + \sin^{-1} \mathfrak{z} - \frac{\pi}{2} \right]$$

where \mathfrak{z} has the same significance as before.

In order that a point $x=x_1$ may be suitable for the above matching in the case $\ell=0$ it is necessary not only that it satisfy (34) but also that \mathfrak{f} be so large that (42) may be a good approximation to (41). (34) can always be satisfied by values of x_1 in the neighborhood of $\frac{3}{2}\pi$. The condition that $J_{\frac{1}{2}}(\mathfrak{f})$ can be replaced by the first term of its asymptotic expansion is

$$(45) \quad \mathfrak{f} \gg \frac{5}{72}$$

Now the maximum value of $\mathfrak{z} \sqrt{1-\mathfrak{z}^2}$ is $\frac{1}{2}$, and $\sin^{-1} \mathfrak{z} < \mathfrak{z}$. Hence

$$(46) \quad \mathfrak{f} > 2\pi \left(\frac{\pi}{2} - \frac{1}{2} - \mathfrak{z} \right) > 2\pi(1-\mathfrak{z})$$

For $x = \frac{3}{2}\eta$, $\beta = \frac{1}{2}\sqrt{\frac{3}{2}}$ and $\lambda(1-\beta) \approx .744$. (45) will then also be satisfied provided

$$(47) \quad \eta \gg \frac{5}{72 \times .744} \approx .090$$

It will be shown later that (47) is indeed satisfied for scattered electrons of small energy with reasonable values of the screening radius

There remains only to substitute (41) for \mathcal{L} in (16), using the values of c and η given by (43). In the subsequent numerical work it proved convenient to have the result expressed in terms of the Bessel function of the second kind instead of the Bessel function of negative order. The Bessel function of the second kind, Y_s , is defined as follows:

$$(48) \quad Y_s(x) = \frac{J_s(x) \cos s\pi - J_{-s}(x)}{\sin s\pi}$$

If (48) written with $s = \frac{1}{3}$ is solved for $J_{-1/3}$ and the result substituted in (41), there results

$$(49) \quad \mathcal{U}_i = \frac{1}{3} \sqrt{3} C Q^{-1/2} \xi^{1/2} [J_{1/3}(\xi) \sin \Delta - Y_{1/3}(\xi) \cos \Delta]$$

with

$$(49a) \quad \Delta = \frac{\pi}{3} - \eta$$

If one differentiates (49) with respect to r , taking equations (29c), (41a), and (39) into account, and evaluates the result at $r = a$ he obtains after some reduction by means of equations (35) and (43c)

$$(50) \quad \left(\frac{d\mathcal{U}_1}{dr}\right)_{r=a}^2 = \frac{\pi}{2} k \xi_0 \left[(M J_{1/2}(\xi_0) - J'_{1/2}(\xi_0)) \sin \Delta - (M Y_{1/2}(\xi_0) - Y'_{1/2}(\xi_0)) \cos \Delta \right]^2$$

where

$$(50a) \quad M = \frac{1}{4\sigma \xi_0^{3/2}} - \frac{1}{2\xi_0}$$

ξ_0 represents the value of ξ when $r=a$, and the primes on the Bessel functions indicate differentiation with respect to their arguments. Similarly (49) reduces for $r=a$ to

$$(51) \quad (\mathcal{U}_1)_{r=a}^2 = \frac{\pi}{2} \cdot \frac{\xi_0}{k} \left[J_{1/2}(\xi_0) \sin \Delta - Y_{1/2}(\xi_0) \cos \Delta \right]^2$$

Substituting (50) and (51) for \mathcal{L}'_0 and \mathcal{L}_0 respectively in (16) we obtain the final result:

$$(52) \quad J_\nu \propto \frac{2}{\pi \xi_0} \left\{ \left[J_{1/2}(\xi_0) \sin \Delta - Y_{1/2}(\xi_0) \cos \Delta \right]^2 + \left[(M J_{1/2}(\xi_0) - J'_{1/2}(\xi_0)) \sin \Delta - (M Y_{1/2}(\xi_0) - Y'_{1/2}(\xi_0)) \cos \Delta \right]^2 \right\}^{-1}$$

From (44), (31c), and (35) we get

$$(53) \quad \xi_0 = \sigma \left\{ \frac{\sin^{-1} \sqrt{\mathcal{E}'}}{\sqrt{1-\mathcal{E}'}} - \sqrt{\mathcal{E}'} \right\}$$

The behavior of (52) for small values of \mathcal{E}' , and hence of ξ_0 , is of special importance. To investigate this expand (53) in a power series. We get

$$(54a) \quad \xi_0 = \frac{2\sigma}{3} \mathcal{E}'^{3/2} \left[1 + 2^2 \cdot 5^{-1} \mathcal{E}' + 2^3 \cdot 3 \cdot 5^{-1} \cdot 7^{-1} \mathcal{E}'^2 + O(\mathcal{E}'^3) \right]$$

This series may be reverted and the result substituted in (50a). This gives

$$(54b) \quad M = -3^{-1} \xi_0^{-1} + 2^{1/2} 3^{-1/3} 5^{-1} \sigma^{-2/3} \xi_0^{-1/3} - 2^{-2/3} 3^{-2/3} 7^{-1} \sigma^{-4/3} \xi_0^{1/3} + O(\xi)$$

By means of (54b) and the power series expansion of the Bessel functions one can now calculate the value of the denominator of (52) for small \mathcal{E} . Treating Δ as a constant one gets

$$(55) \quad \xi_0 \left\{ [J_{1/3}(\xi_0) \sin \Delta - Y_{1/3}(\xi_0) \cos \Delta]^2 + [(M J_{1/3}(\xi_0) - J'_{1/3}(\xi_0)) \sin \Delta - (M Y_{1/3}(\xi_0) - Y'_{1/3}(\xi_0)) \cos \Delta]^2 \right\} = A^2 \xi_0^{-1/3} + [2AB + \frac{2^{2/3} 3^{-1}}{\Gamma(2/3)} \cos^2 \Delta] \xi_0^{1/3} + O(\xi_0)$$

with

$$(55a) \quad A = \left(\frac{2^{5/3} 3^{-5/6} 5^{-1} \sigma^{-2/3}}{\Gamma(2/3)} + \frac{2^{2/3} 3^{-2/3}}{\Gamma(4/3)} \right) \cos \Delta - \frac{2^{2/3} 3^{-1}}{\Gamma(4/3)} \sin \Delta$$

$$(55b) \quad B = - \left(\frac{3^{-5/6} 5^{-1} \sigma^{-2/3}}{\Gamma(4/3)} + \frac{2^{-1} 3^{-7/6} 7^{-1} \sigma^{-4/3}}{\Gamma(2/3)} \right) \cos \Delta + \frac{3^{-1/3} 5^{-1} \sigma^{-2/3}}{\Gamma(4/3)} \sin \Delta$$

In case A approaches some value different from zero as ξ_0 and \mathcal{E} approach zero, it is seen that the denominator of (52) becomes infinite like $\xi_0^{-1/3}$ or like $\mathcal{E}^{-1/2}$ and hence that the intensity approaches zero like $\mathcal{E}^{1/2}$. But in case A approaches zero as \mathcal{E} approaches zero more discussion is necessary. If we represent by Δ_0 the limiting value of Δ as ξ_0 approaches zero, this case occurs when

$$(56) \quad \tan \Delta_0 = 3^{1/3} + \frac{2 \cdot 3^{1/6} \cdot \Gamma(4/3)}{5 \cdot \Gamma(2/3) \cdot \sigma^{1/3}}$$

or when

$$(56a) \quad \Delta_0 = \alpha \pi + \pi$$

where α is a number less than $\frac{1}{2}$ defined by (56) and \mathcal{E} is

any integer. A numerical evaluation of (56) shows that for reasonable values of σ the second term on the right is small compared to the first; for $\sigma = 8$, for example, the second term is less than six per cent. of the first. Hence we have approximately

$$(56b) \quad \alpha \approx \frac{1}{\pi} \tan^{-1} \sqrt[3]{3} = .307.$$

From (43d), (35d), and (49a) we have

$$(57) \quad \Delta_0 = \frac{\pi}{3} + \pi \left(\frac{\sigma}{2} - 1 \right)$$

which together with (56a) shows that the singular case occurs when

$$(58) \quad \sigma = 2s' + 2\alpha - \frac{2}{3}$$

where s' is an integer. With the value (56b) for α this is

$$(58a) \quad \sigma = 2s' - .053.$$

In order to find the behavior of J_ν in the singular case note that when (56) is satisfied $\left(\frac{dA}{d\Delta} \right)_{\xi=0}$ cannot vanish and that therefore $A = O(\Delta - \Delta_0)$. In the same way that (57) was obtained one can get

$$(58) \quad \Delta = \frac{\pi}{3} + \pi \left(\frac{\sigma}{2\sqrt{1-\xi}} - 1 \right).$$

From this equation it follows that as \mathcal{E} approaches zero $\frac{dA}{d\mathcal{E}}$ remains finite and hence $\Delta - \Delta_0 = O(\mathcal{E}) = O(\xi^{\frac{2}{3}})$. Therefore in this case $A^2 = O(\xi^{\frac{4}{3}})$ and the first term in (55) is infinitesimal

of the first order with ξ . The second term of (55) appears, therefore, to be the term of lowest order as indeed it is since $\cos^2 \Delta_0$ cannot vanish because of (56). Hence in the singular case defined by (58), $J_\nu = O(\xi^{-\frac{1}{2}}) = O(\mathcal{E}^{-\frac{1}{2}})$; that is, J_ν becomes infinite like $\frac{1}{\sqrt{\mathcal{E}}}$.

The choice of the parameters Z and a and the general behavior of the function (52) remain yet to be considered. These will be discussed in section 3.

Part IIISection 2 Model Number 2

M. F. Manning²⁵⁾ has discussed the question of what forms of the potential energy function lead to a one-dimensional Schrödinger equation solvable by means of a recursion formula of two or three terms. Among the potential functions which he finds to lead to a Schrödinger equation of the hypergeometric type is

$$(1) \quad V = \frac{e^{-\frac{r}{a}}}{1 - e^{-\frac{r}{a}}}.$$

For small r , V represents an approximately Coulomb field, since we have

$$(1a) \quad V = A \left[\frac{a}{r} - \frac{1}{2} + o(r) \right];$$

while for large r , V goes exponentially to zero. It is thus suitable roughly to represent the potential for a screened Coulomb field. From (1a) it is seen that in order that V may approximately represent the potential of an atom of atomic number Z , A must be chosen according to the equation

$$(1b) \quad A = -\frac{Z}{a}$$

where again Hartree atomic units are being used.

With the potential (1) the radial Schrödinger equation for an electron with the angular momentum zero is

$$(2) \quad \frac{d^2 L}{dr^2} + \left(k^2 + \frac{2Z}{a} \cdot \frac{e^{-r/a}}{1 - e^{-r/a}} \right) L = 0$$

Here, as in section 1, k^2 is twice the energy of the electron. If the following change of independent variable is made:

$$(3) \quad x = e^{-r/a}$$

equation (2) becomes

$$(4) \quad \frac{d}{dx} x \frac{dL}{dx} + \left(\frac{\kappa^2}{x^2} + \frac{\sigma^2}{1-x} \right) L = 0$$

where

$$(4a) \quad \kappa^2 = k^2 a^2$$

$$(4b) \quad \sigma^2 = 2Za$$

If one now writes in equation (4)

$$(5) \quad L = A x^{i\kappa} y$$

where i is the imaginary unit and A is an arbitrary constant, there results

$$(6) \quad x(1-x) \frac{d^2 y}{dx^2} + (2i\kappa + 1)(1-x) \frac{dy}{dx} + \sigma^2 y = 0$$

This is the standard form for the hypergeometric equation²⁶⁾ with the parameters α , β , γ , where

$$(7) \quad \begin{aligned} \alpha &= i\kappa + R \\ \beta &= i\kappa - R \\ \gamma &= 2i\kappa + 1 \end{aligned}$$

with

$$(8) \quad R = \sqrt{\sigma^2 - \kappa^2}$$

Besides the solution $y = F(\alpha, \beta; \gamma; x)$ where F is the hypergeometric function, equation (6) has the solution

$$(9) \quad y = (1-x)^{\delta-\alpha-\beta} F(\delta-\beta, \delta-\alpha; 1+\delta-\alpha-\beta; 1-x)$$

$$= (1-x) F(i\kappa+1+R, i\kappa+1-R; 2; 1-x)$$

As r approaches zero, x approaches one; and since under these circumstances the right side of (9) approaches zero, it is seen that (9) is the solution required to fit the boundary conditions at $r=0$. From (5) and (9) we get

$$(10) \quad L = A(1-x)x^{i\kappa} F(i\kappa+1+R, i\kappa+1-R; 2; 1-x)$$

The general formula

$$(11) \quad F(\alpha, \beta; \gamma; x) = \frac{\Gamma(\gamma)\Gamma(\delta-\alpha-\beta)}{\Gamma(\gamma-\alpha)\Gamma(\gamma-\beta)} F(\alpha, \beta; \alpha+\beta-\delta+1; 1-x)$$

$$+ \frac{\Gamma(\delta)\Gamma(\alpha+\beta-\delta)}{\Gamma(\alpha)\Gamma(\beta)} F(\delta-\alpha, \delta-\beta; \delta-\alpha-\beta+1; 1-x)$$

holds when $0 < x < 1$ and $\delta - \alpha - \beta$ is not an integer.²⁶⁾ For the hypergeometric function in (10) the quantity corresponding to $\delta - \alpha - \beta$ is $-2i\kappa$, which is not an integer. Hence (11) is applicable to that function, and it gives

$$(12) \quad F(i\kappa+1+R, i\kappa+1-R; 2; 1-x) = \frac{\Gamma(2)\Gamma(-2i\kappa)}{\Gamma(1-R-i\kappa)\Gamma(1+R-i\kappa)} F(i\kappa+1+R, i\kappa+1-R; 1+2i\kappa; x)$$

$$+ \frac{\Gamma(2)\Gamma(2i\kappa)}{\Gamma(1+R+i\kappa)\Gamma(1-R+i\kappa)} x^{-2i\kappa} F(1-R-i\kappa, 1+R-i\kappa; 1-2i\kappa; x).$$

Were it not for the factor $x^{-2i\kappa}$ in the second term, the second term on the right side of (12) would be the complex conjugate of the first term when x is real. Substituting

(12) in (10) we get

$$(13) \quad L = A(1-x) \left\{ \frac{\Gamma(2)\Gamma(-2i\kappa)}{\Gamma(1-R-i\kappa)\Gamma(1+R-i\kappa)} x^{i\kappa} F(1+R+i\kappa, 1-R+i\kappa; 1+2i\kappa; x) \right. \\ \left. + \text{complex conjugate} \right\}.$$

This equation shows that L is real as it stands with a real value of A .

Noting that $F(\alpha, \beta; \gamma; x) = 1 + O(x)$, we find, on replacing x by $e^{-\frac{r}{a}}$ in (13), that

$$(14) \quad L = A(1-x) \left\{ M e^{-ikr+i\varphi} [1+O(x)] + \text{complex conjugate} \right\} \\ = 2AM \cos(kr-\varphi) + O(x)$$

where

$$(15a) \quad M = \left| \frac{\Gamma(2)\Gamma(-2i\kappa)}{\Gamma(1-R-i\kappa)\Gamma(1+R-i\kappa)} \right|$$

$$(15b) \quad \varphi = 2\text{arg} \left\{ \frac{\Gamma(2)\Gamma(-2i\kappa)}{\Gamma(1-R-i\kappa)\Gamma(1+R-i\kappa)} \right\}$$

Thus, L will be normalized in accordance with equation (21) of part II section 3 provided

$$(16) \quad A = \frac{1}{2kM}$$

For small r , x is near unity, and from (3), $1-x = \frac{r}{a} + O(r^2)$. Hence, by (10), $L = A\frac{r}{a} + O(r^2)$. Thus the function $\frac{1}{A}L$ is normalized in accordance with the requirements stated on page 46, and according to the argument given in section 1 the intensity should be proportional to $k|A|^2$ for sufficiently small k . Thus we have

$$(17) \quad J_\nu \propto \frac{1}{kM^2}$$

The gamma functions with complex arguments in equation (15a) can be evaluated in a way described by Nielson²⁷⁾ with the result

$$(18) \quad \frac{1}{M} = \frac{\sigma \sqrt{a} \sqrt{2\pi\kappa} \sinh 2\pi\kappa}{\sqrt{\cosh 2\pi\kappa - \cos 2\pi R}}$$

Substituting (18) in (17) we get, after dividing by the constant $4\pi\sigma^2 a$

$$(19) \quad J_\nu \propto \frac{\sinh 2\pi\kappa}{\cosh 2\pi\kappa - \cos 2\pi R}$$

For large κ (large energy), the hyperbolic sine and cosine are large and nearly equal; and if R is still real so that $\cos 2\pi R$ is not also large, it is seen that the right side of (19) is practically unity.

For small energy, (19) may be expanded in a power series in κ . There results

$$(20) \quad J_\nu \propto \frac{2\pi\kappa + O(\kappa^3)}{1 - \cos \pi\sigma + 2\pi^2\kappa^2 \left(1 - \frac{\sin \pi\sigma}{4\pi\sigma}\right) + O(\kappa^4)}$$

Hence if σ is not an even integer, $J_\nu = O(\kappa) = O(\mathcal{E}^{1/2})$; while if σ is an even integer $J_\nu = O(\kappa^{-1}) = O(\mathcal{E}^{-2})$. Thus, as in the previous case, J_ν either becomes zero like the square root of the energy, or becomes infinite like the reciprocal of the square root of the energy, depending on the value of σ .

The choice of the parameters Z and a and the significance of formula (19) will be discussed in the next section.

Part III

Section 3 Choice of Parameters and Discussion of Results

In order intelligently to assign values to the parameters σ and a appearing in the formulae for the intensity of radiation derived in the preceding two sections, it is necessary to compare the potential functions assumed there with some better approximation to the actual atomic field of part II section 2. The best available approximation is the self-consistent field of Hartree; but the statistical approximation of Fermi and Thomas²⁸⁾ is more than sufficiently accurate for the present purpose. This approximation leads to the following formula for the electric potential V_F in atomic units at a distance r atomic units from the nucleus of an atom of atomic number Z :

$$(1) \quad V_F = \frac{Z}{r} \varphi\left(\frac{r}{\mu}\right)$$

where $\varphi(x)$ satisfies the differential equation

$$(2) \quad \frac{d^2\varphi}{dx^2} = \frac{\varphi^{3/2}}{x^2}$$

with the boundary conditions $\varphi(0) = 1$, and $\varphi(\infty) = 0$; and

$$(3) \quad \mu = \sqrt[3]{\frac{9\pi^2}{128Z}} = 0.885 Z^{-1/3}$$

The function φ has been tabulated by Fermi²⁸⁾ and will be found plotted at the end of this section.

The potential of model number 2 may be written

$$(4) \quad V_2 = \frac{Z}{r} \cdot \frac{r/a}{e^{r/a} - 1}$$

so that the functions $\varphi(\frac{r}{a})$ and $\frac{r/a}{e^{r/a} - 1}$ are to be compared. Both functions are plotted on the same graph, and it is seen that they do not differ greatly in shape, although the function $\frac{rV_2}{Z}$ goes to zero much more rapidly as r increases than does $\varphi(\frac{r}{a})$. In each case the function $\varphi(\frac{r}{a})$ or $\frac{rV_2}{Z}$ represents the ratio of the potential in the atom at the distance r from the nucleus to the potential at the same distance from a bare nucleus. It would, then, seem reasonable to choose a so that the two functions would be equal at that value of r for which their values are about one-half; that is, so that half the potential of the nucleus would be screened off at about the same distance in each case. One may thus define a as a function of y by requiring that $\varphi(\frac{r}{a})$ be equal to $\frac{r/a(y)}{e^{r/a(y)} - 1}$ for that value of r for which they are both equal to y . It is more convenient to consider the function $N(y) = a(y)/\mu$. This function will be found plotted at the end of this section. From section 2 we have $\sigma = \sqrt{2Za}$; whence, with the definition of N and equation (3) it follows that

$$(5) \quad \sigma = Z^{1/2} \sqrt{1.77N}$$

With values of y ranging from 0.2 to 0.8, and with 74, the atomic number of tungsten, for Z , (5) gives values for σ ranging from about 5.28 to 3.57. Curves showing the intensity

of the x-rays calculated from the formula of section 2 using various values of σ in the neighborhood of the above values plotted against the relative energy \mathcal{E} (defined in sections 1 and 2) and the actual energy \mathcal{E} of the scattered electron will be found at the end of this section.

The potential V_1 adopted for the calculations of section 1 is defined as follows:

$$(6) \quad V_1 = \begin{array}{ll} \frac{Z}{r} \left(1 - \frac{r}{a}\right) & \text{for } r < a \\ 0 & \text{for } r > a \end{array}$$

Again one may choose for Z the atomic number of the element composing the target in which he is interested - in the present case, tungsten - and compare the function $1 - \frac{r}{a}$ with the function $\varphi\left(\frac{\mathcal{E}}{\mu}\right)$ as was done above for V_2 . The function $1 - \frac{r}{a}$, however, is represented graphically as a straight line and is very different in shape from the function $\varphi\left(\frac{\mathcal{E}}{\mu}\right)$; and the process does not carry the conviction that it did in the previous case. Nevertheless, if one compares the two functions in this manner he finds values for σ from about 8 to 5.6. At the end of this section will be found curves showing the x-ray intensity calculated from the formula of section 1 with such values of σ plotted again against both \mathcal{E} and \mathcal{E} . These curves, it will be noticed, are not greatly dissimilar in shape to those drawn from the formula of section 2; but the scales of abscissae, both in the case in which the abscissae represent \mathcal{E} and

in that in which they represent E , are quite different. This difference in the case in which the abscissae represent \mathcal{E} is not surprising because the parameter \mathcal{E} is itself relative to the model adopted; but when the abscissae represent E , this difference in scale represents an actual difference in the experimental results predicted by the two models. Specifically, model number 1 with the above values for the parameters predicts that such characteristics of the intensity curve as maxima or the settling down to a constant value will occur at much higher energies of the scattered electron, that is, at x-ray frequencies much more removed from the high frequency limit, than does model number 2.

Since the discrepancy in the scale must be due to an inappropriate choice of the parameters of the model in at least one of the two cases, and since the choice in the case of model number 2 seems quite appropriate, we may expect the difficulty to be resolved by the proper choice of the parameters for model number 1. Now in their discussion of the Ramsauer effect, Allis and Morse²⁹⁾ have used the same model of the atom that we have used in section 1, and they found that they got a surprisingly good agreement with experiment when they chose their parameters in a way quite different from that in which we have chosen ours. They based their choice of parameters on a model of the atom due to Slater.³⁰⁾ Slater assumed hydrogenic S-state wave functions for all the electrons in the atom with, however,

different amounts of screening for the electrons in different shells. He then set up simple rules for determining the screening constants for the different shells in such a way as to give roughly correct values for such observable things as ionization potentials and x-ray energy levels. With this model it is possible to calculate the charge density at any distance from the nucleus due to the electrons in any given shell. Allis and Morse then considered the field which results when one considers the charge of all the electrons in one shell as spread uniformly over the sphere which occupies the position of maximum radial charge density for the shell considered. If one denotes the potential of this field by V then rV when plotted against r gives a broken line which meets the axis of ordinates in Z , the atomic number of the element, suffers an increase in slope whenever r passes through an electron shell, and meets the axis of abscissae at r_0 , the radius of the outermost shell. They then chose for their screening radius, corresponding to our a , the value r_0 , and for their parameter corresponding to our σ such a value as would make

$$\int_0^{r_0} rV_1 dr = \int_0^{r_0} rV dr.$$

This of course makes the parameter Z appearing in V_1 less than the atomic number of the element considered.

It might seem at first inadvisable to choose for our calculations values of the parameters which will make the field close to the nucleus very different from the actual

atomic field there, for it is the region of high field near the nucleus which is important in the production of high frequency x-rays. It must be remembered, however, that what we are at present calculating directly is not the rate of production of x-rays but the probability that a slow electron will be reflected by the field of the atom. This does not depend so specifically on the inner regions of the field as does the actual production of x-rays; and indeed we should expect it to depend on the same things that the scattering of slow electrons depends on. If the parameters are chosen for the tungsten atom after the manner of Allis and Morse, the following values are found: $\alpha = 5.11$, $\sigma = 12.3$, $Z = 14.8$. These values are indeed very different from those given by the previous choice, which gave a value of about $1/3$ for α . This choice, however, again gives a discrepancy in scale between the two models, but this time in the opposite direction. An intermediate choice here, namely, of about 2 for α and the same values (around 12) for σ , gives agreement. Inasmuch as the scale is not as sensitive to the choice of the parameters for model number 2 as it is for model number 1, and since the potential for model number 2 more closely approximates that for the actual atom than does that for model number 1, it seems probable that the intermediate choice of parameters corresponds the most closely to reality.

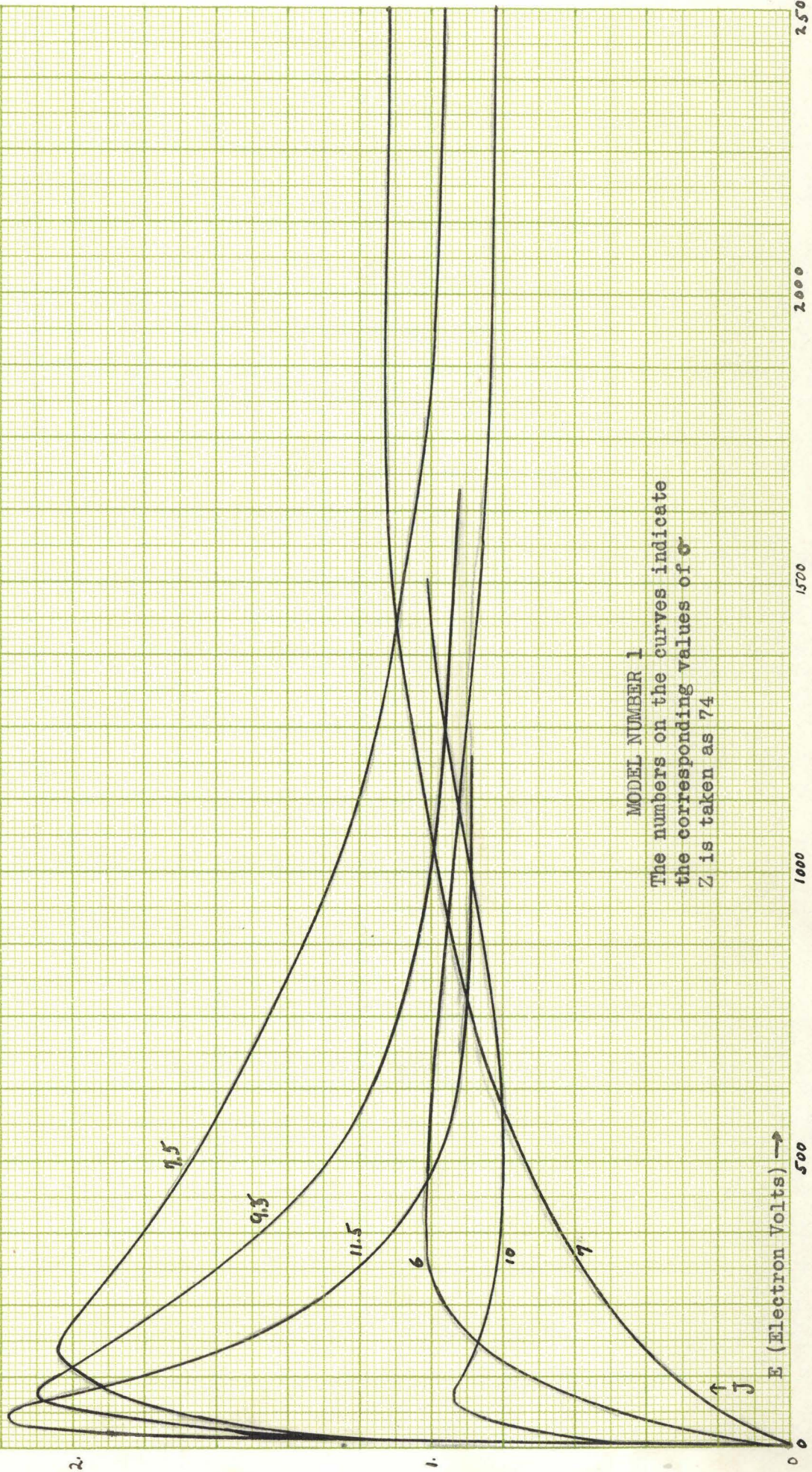
The condition for the validity of the W.K.B. approximation used in the calculations of section 1 is given by

equation (47) of that section. A comparison of this equation with equation (35e) of the same section shows that this condition is that σ be much larger than $1/5$. This condition is very well satisfied for all the values of the parameters proposed in this section.

On examining the curves showing the theoretical intensity of x-rays which will be found at the end of this section, one will see that their shape is strongly dependent on σ . As the energy of the scattered electron approaches zero, that is, as the frequency of the x-rays approaches the Duane-Hunt limit, the intensity either falls smoothly to zero or it rises to a maximum at from a few volts to a few tens of volts from the limit and then falls rapidly to zero. This maximum, when it is present, is due to resonance of the scattered electron with a virtual energy level of the atom; for by definition a virtual energy level is an energy for which the wave function of an electron has a large amplitude inside the atom, and it is this condition that we have shown to govern the emission of the x-rays in which we are interested. Since only P to S transitions are important in producing these x-rays, only virtual S-levels can cause the maxima which appear in our curves; and the general shape of these curves shows that only that virtual S-level of lowest energy is effective. If there is a virtual S-level of exactly zero energy, then, as was shown in sections 1 and 2, the intensity of the x-rays approaches infinity as the energy of the

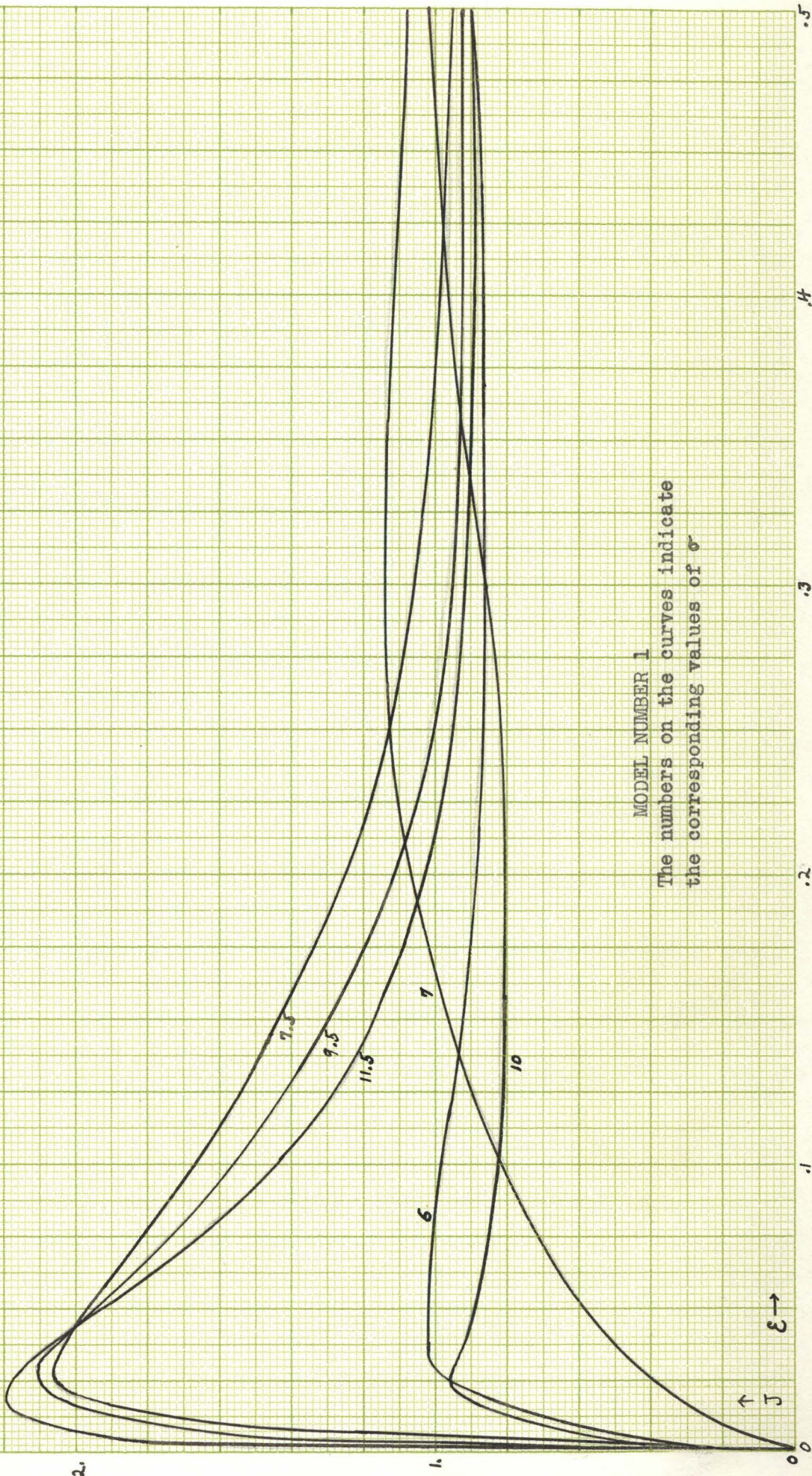
scattered electron approaches zero. The fact that only the virtual energy levels of angular momentum zero affect noticeably the distribution of energy in the continuous x-ray spectrum probably renders impossible any correlation between this distribution of energy and the cross section for scattering by the atom of slow electrons; for in the latter process in the case of heavy atoms, the virtual energy levels of angular momentum different from zero play a large role.²⁹⁾

The distribution of energy in Bremsstrahlung as calculated in sections 1 and 2 is very sensitive to the form of the function used approximately to represent the field of the atom, and it seems, therefore, impractical by a reasonable improvement in the model to predict for which elements the sharp maximum in the energy density near the Duane-Hunt limit will occur and for which it will not. All that can be said from the present calculations and, it would seem, also from any reasonably simple improved calculations of the same type, is that for some elements such a maximum of intensity should be observed very close to the high frequency limit and for others the intensity should fall smoothly to zero in a range of about a hundred volts.



MODEL NUMBER 1

The numbers on the curves indicate
the corresponding values of σ
Z is taken as 74

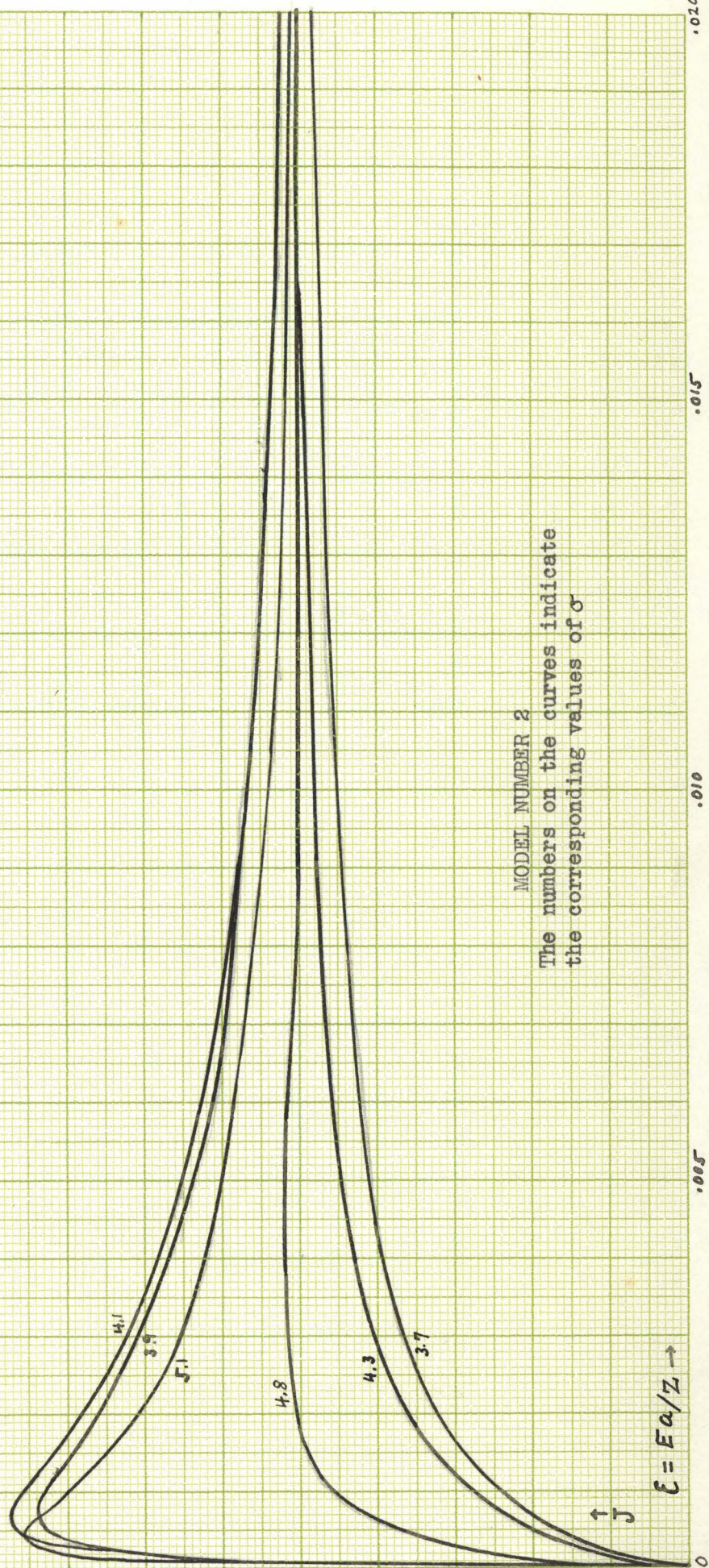


MODEL NUMBER 1
 The numbers on the curves indicate
 the corresponding values of σ

2.

1.

0



MODEL NUMBER 2

The numbers on the curves indicate the corresponding values of σ

$\xi = E a / Z \rightarrow$

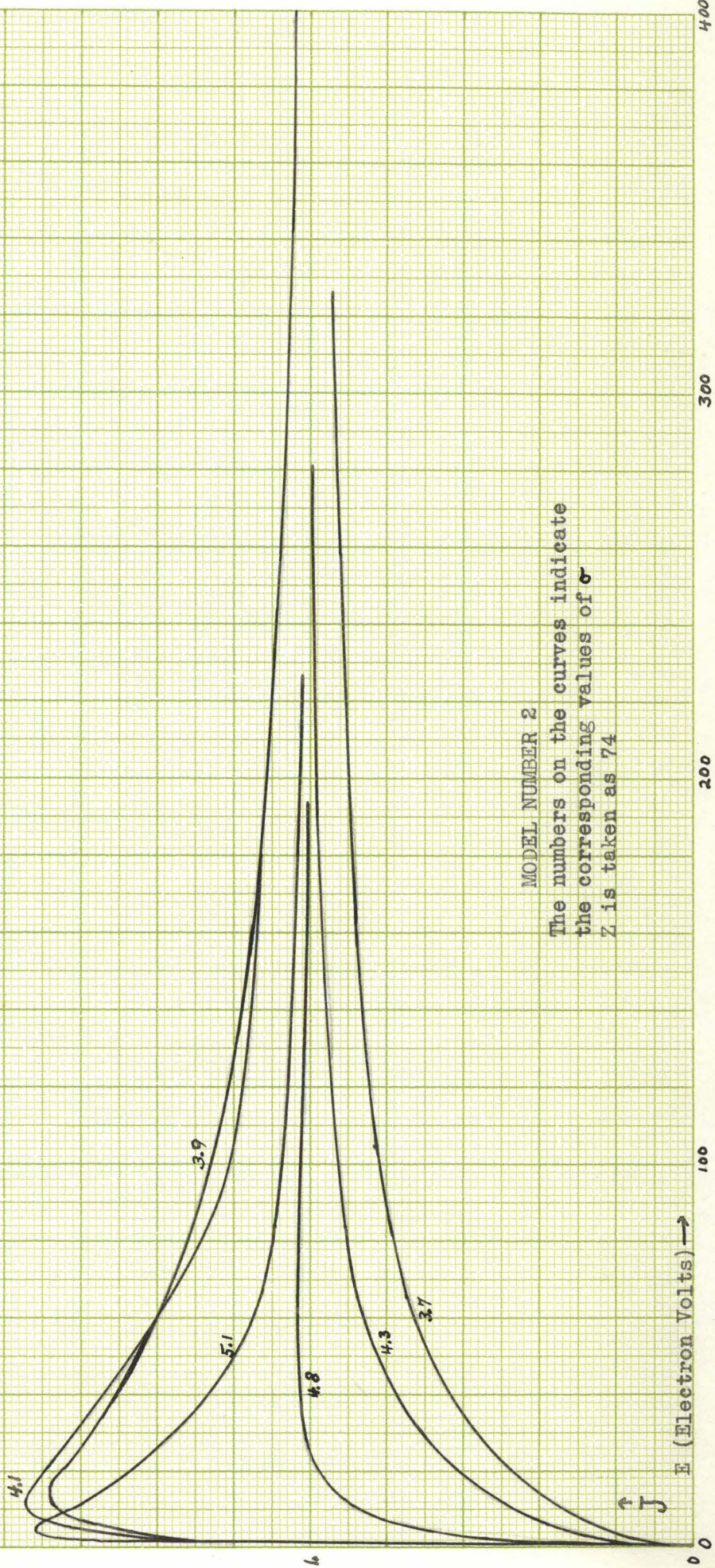
$\uparrow J$

.005

.010

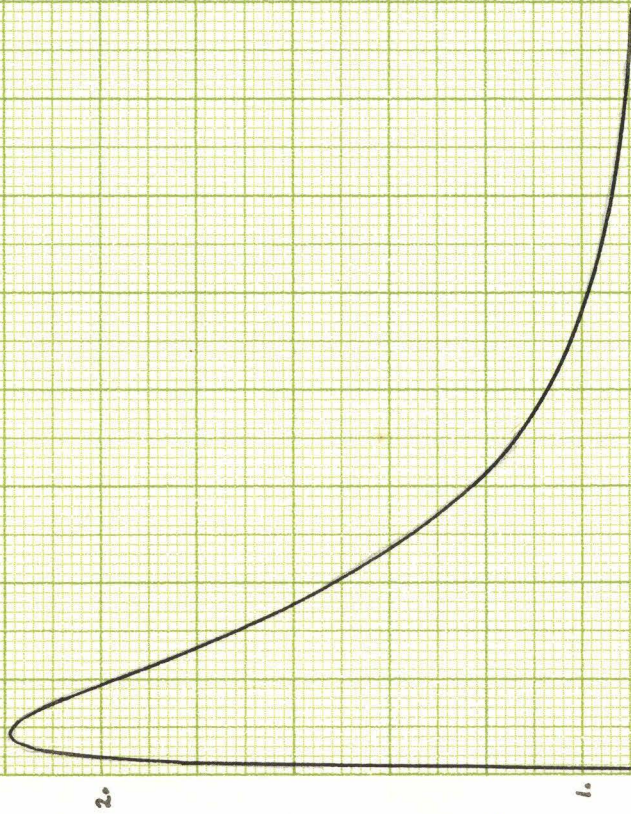
.015

.020



MODEL NUMBER 2

The numbers on the curves indicate the corresponding values of σ Z is taken as 74



MODEL NUMBER 1

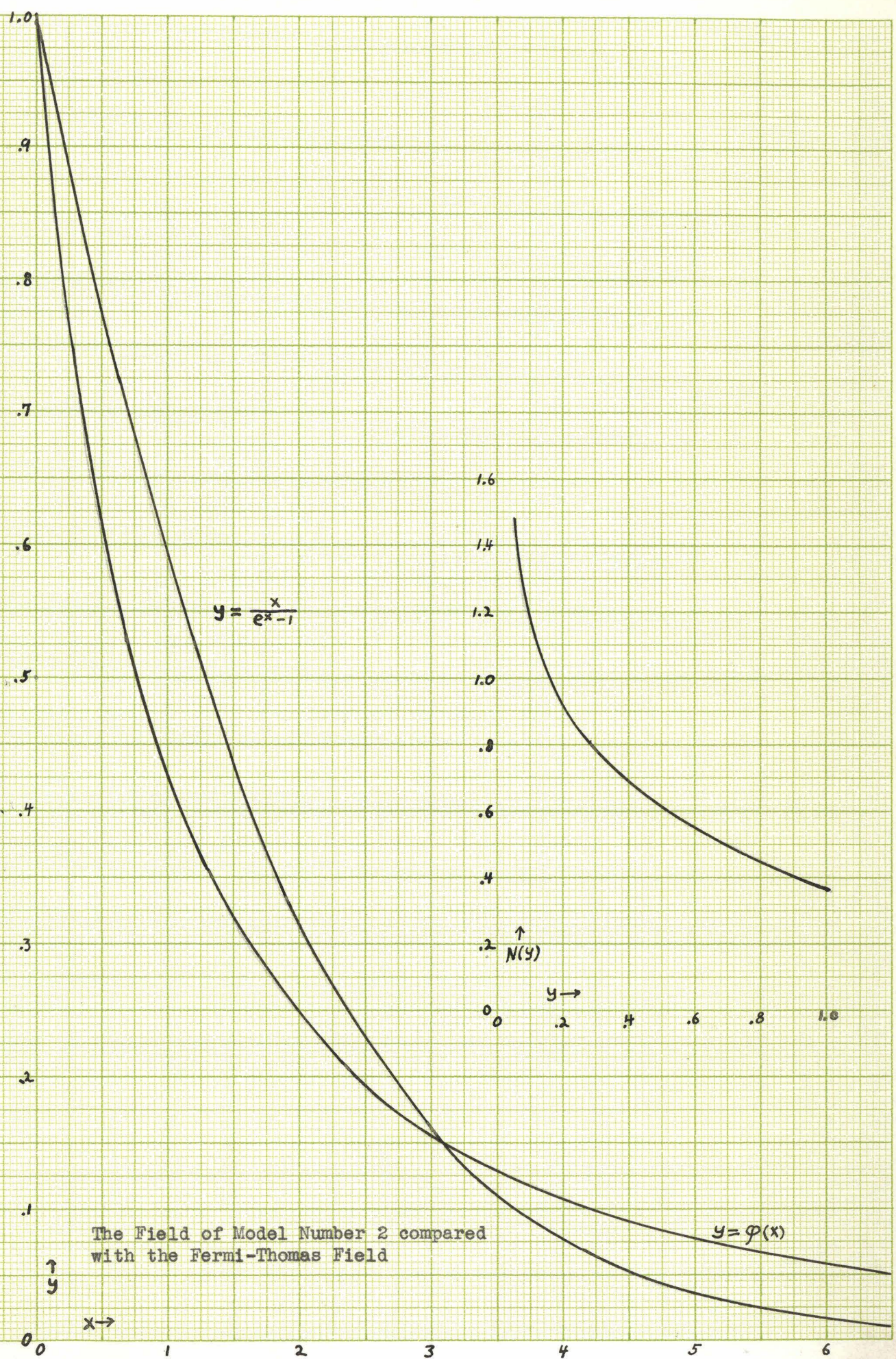
$\sigma = 11.5$

Z = 2

E (Electron Volts) →

100

200



The Field of Model Number 2 compared with the Fermi-Thomas Field

↑
y

x →

$$y = \frac{x}{e^x - 1}$$

$$y = \varphi(x)$$

↑
N(y)

y →

Part IV Comparison with Experiment

The spectral distribution of energy in Bremsstrahlung is usually investigated by allowing the radiation from an x-ray tube to pass through a spectrometer and measuring the ionization produced in a suitable chamber by the radiation that gets through. One may hold the potential on the tube constant and vary the setting of the spectrometer, thus measuring directly the amount of energy present in the Bremsstrahlung in various frequency ranges. More frequently, however, one keeps the setting of the spectrometer fixed and varies the potential on the x-ray tube; the resulting curves of ionization plotted against tube voltage are called isochromats. In either case there are at least two circumstances which cause the resulting curves to differ from those expressing the distribution of energy in the radiation produced by the collision of an electron with an atom: First, the target of the x-ray tube is thick; and, as the incident electrons are gradually slowed down as they penetrate more deeply into it, we receive from various depths in the target radiation produced by electrons of various energies. And second, the spectrometer itself is not completely opaque to radiation of frequencies other than that for which it is set.

The most recent and perhaps the most precise measurements of this nature are those of Du Mond and Bollman.⁶⁾ Using a double-crystal spectrometer and measuring only close

to the Duane-Hunt limit, these workers have obtained two isochromats, one with potentials in the neighborhood of 20,000 volts on the tube and one with tube potentials near 10,000 volts. In discussing such experiments it is convenient - at least for the present purpose - not to discuss the isochromats themselves, but rather to discuss their derived curves; for in the latter the most important effects of the thickness of the target are eliminated, and any small peculiarities of the energy distribution appear to better advantage. Accordingly, at the end of this section will be found a curve showing the rate of change, I' , of the ionization current with respect to the potential on the x-ray tube plotted against a linear function, ω , of this potential for the 20,000 volt isochromat obtained by Du Mond and Bollman. The function ω is so adjusted that it vanishes for that value of the tube potential which corresponds according to Du Mond and Bollman to the Duane-Hunt limit and that a change of one unit in ω corresponds to a change of 16.8 volts in the tube potential. The reason for this latter adjustment will appear later. The most striking characteristic of this curve is the pronounced maximum which occurs near $\omega = 0$. This maximum corresponds to a slight bend or knee in the isochromat itself and was totally unexpected. While the fillet extending far below the limiting potential is almost certainly due to the finite resolving power of the spectrometer, the maximum in the derived curve must be due

to some characteristic of the energy distribution in the Bremsstrahlung itself. Although it is conceivable that this may be in some way connected with the structure of the target as a solid body, no very convincing explanation along these lines has been offered; and since it was seen in part III that the screening of the nuclear field by the extra nuclear electrons can have a very marked effect on the energy distribution in the Bremsstrahlung from a single atom, it is natural to look for the explanation in this effect.

Before the results of part III can be compared with the experiments, it is necessary to take account of the thickness of the target and of the finite resolving power of the spectrometer. In the following let all energies and frequencies be expressed in the same unit by means of the relation energy equals frequency times Plank's constant. The energy, $J_\nu d\nu$, in the Bremsstrahlung from a single atom in the frequency range from ν to $\nu+d\nu$ is a function both of the energy, \varkappa , of the incident cathode rays and of the frequency, ν . There is both theoretical and experimental evidence that J_ν is nearly independent of ν and nearly inversely proportional to \varkappa for frequencies near the limiting frequency $\nu = \varkappa$ but not too near it. The dependence of J_ν on $\varkappa - \nu$, the energy of the scattered electron, has been calculated in part III. As we are interested only in frequencies near the limiting frequency, the exact dependence on \varkappa is not important, and we may

write

$$(1) \quad \bar{J}_\nu = \frac{1}{\bar{x}} f(x-\nu)$$

If, now, it is assumed that the electrons incident on the target with the energy \bar{x}_0 are slowed down in such a way that at the depth ξ in the target they all have the same energy $\bar{x}(\xi)$, and if the absorption of the x-rays by the target is neglected, we may expect to receive from depths from ξ to $\xi+d\xi$ in the target radiation of energy proportional to

$$d\bar{J}_\nu = \frac{1}{\bar{x}(\xi)} f[\bar{x}(\xi)-\nu] d\xi$$

and the energy per unit frequency range received from the whole target will be

$$(2) \quad \bar{J}_\nu = \int_0^\infty \frac{1}{\bar{x}(\xi)} f[\bar{x}(\xi)-\nu] d\xi = \int_{\bar{x}_0}^\nu \frac{1}{\bar{x}} f(x-\nu) \frac{d\xi}{d\bar{x}} d\bar{x}$$

The integration may be stopped at $\bar{x}=\nu$ because $f(x-\nu)$ vanishes for smaller \bar{x} . If we assume that the Thomson-Whiddington law³¹⁾ adequately describes the slowing down of the electrons in the target, we have $\frac{d\xi}{d\bar{x}} \propto -\bar{x}$, and

$$(3) \quad \bar{J}_\nu = \int_\nu^{\bar{x}_0} f(x-\nu) d\bar{x} = \int_0^{\bar{x}_0-\nu} f(x) dx$$

The spectrometer may be supposed to transmit the fraction $g(\nu_0, \nu)$ of the incident radiation of frequency ν when it is set for the frequency ν_0 . The experimental isochromat will then be given by

$$(4) \quad I_{\nu_0} = \int_0^\infty g(\nu_0, \nu) \bar{J}_\nu d\nu = \int_0^\infty g(\nu_0, \nu) d\nu \int_0^{\bar{x}_0-\nu} f(x) dx$$

and

$$(4a) \quad I'_{\nu_0} = \int_0^{\infty} g(\nu_0, \nu) f(\bar{z}-\nu) d\nu = \int_0^{\bar{z}} g(\nu_0, \bar{z}-x) f(x) dx.$$

The dependence of I'_{ν_0} on the upper limit of integration, \bar{z} , is weak because ν_0 is a high frequency, and $g(\nu_0, 0)$ may be supposed to be very small. Hence the upper limit \bar{z} in (4a) may be replaced by ∞ . This amounts to integrating over negative frequencies, which is nonsensical; but if the function chosen as an analytic representation of g approaches zero sufficiently rapidly, no great error will be introduced in this way. Further, if g is of the form $g(\nu_0-\nu)$ (4a) takes the simpler form

$$(5) \quad I'_{\nu_0} = \int_0^{\infty} g(w-x) f(x) dx$$

where $w = \bar{z} - \nu_0$ gives directly the distance from the Duane-Hunt limit of the frequency to which the spectrometer is set, and the upper limit of integration has been replaced by ∞ .

Du Mond and Bollman found that the transmission coefficient of their spectrometer is given rather accurately by

$$(6) \quad g(\nu-\nu_0) = \left[1 + \left(\frac{\nu-\nu_0}{a} \right)^2 \right]^{-1}$$

where a is a constant for any given setting of the spectrometer. For the setting of the spectrometer corresponding to their 20,000 volt isochromat, the value of a is 16.8

electron volts. If energies and frequencies are measured in units of 16.8 electron volts, we should have for the case of the 20,000 volt isochromat of Du Mond and Bollman

$$(7) \quad I'_\nu = \int_0^\infty \frac{f(x) dx}{1+(w-x)^2}$$

In evaluating the integral (7) there is no need to replace $f(x)$ by the complicated functions found in part III as these are only approximate anyway. Any simple function which is not too different from those of part III may be used in place of these for $f(x)$ in (7). If one puts

$$(8a) \quad \begin{aligned} f(x) &= 0 & \text{for } x < 0 \\ f(x) &= \alpha & \text{for } 0 < x < \beta \\ f(x) &= 1 & \text{for } \beta < x \end{aligned}$$

or

$$(8b) \quad \begin{aligned} f(x) &= 0 & \text{for } x < 0 \\ f(x) &= \frac{1-\alpha}{\beta} x + \alpha & \text{for } 0 < x < \beta \\ f(x) &= 1 & \text{for } \beta < x \end{aligned}$$

in (7), he obtains respectively

$$(9a) \quad (I'_\nu)_1 = \frac{\pi}{2} + \alpha \tan^{-1} w - (\alpha-1) \tan^{-1}(w-\beta)$$

and

$$(9b) \quad \begin{aligned} (I'_\nu)_2 &= \frac{\pi}{2} + \tan^{-1}(w-\beta) + \frac{\alpha-1}{2\beta} \log \frac{1+(w-\beta)^2}{1+w^2} \\ &+ \left[\alpha - \frac{w}{\beta} (\alpha-1) \right] \left[\tan^{-1} w - \tan^{-1}(w-\beta) \right]. \end{aligned}$$

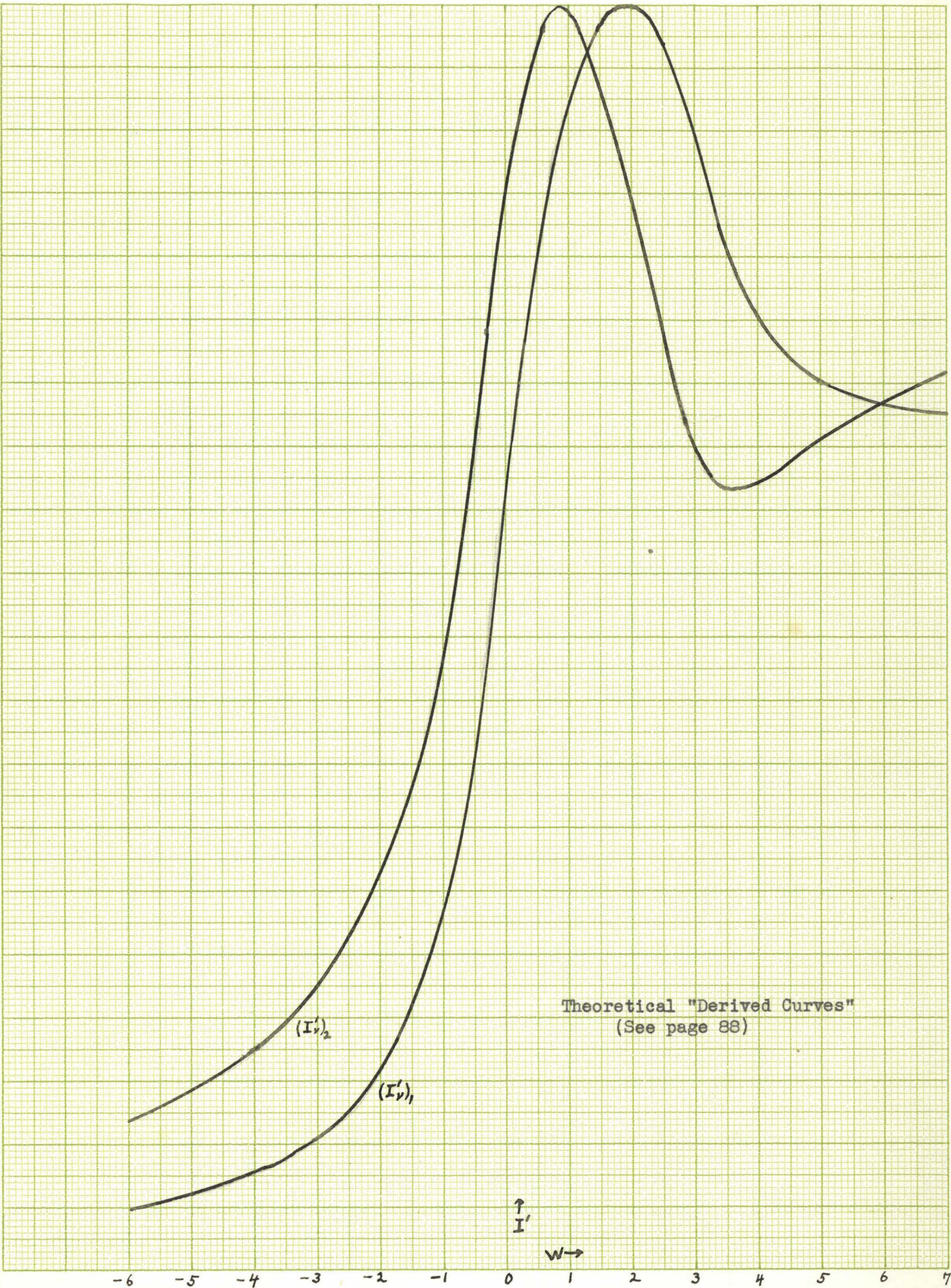
Putting $\alpha=1$ or $\beta=0$ in (9a) or (9b) gives

which increases monotonically, giving no maximum. If one compares (8a) and (8b) with the curves at the end of part III section 3 and remembers that in (8) energies are measured in units of 15.8 electron volts, he will find that a reasonable agreement between $f(x)$ in (8) and the corresponding functions calculated in part III can be obtained by choosing values around 2 for α and between 3 and 7 for β .

The functions $(I'_\nu)_1$ and $(I'_\nu)_2$ given by (9) will be found plotted for the values $\alpha=2$ and $\beta=3$ at the end of this section. On comparing these curves with the experimental curve it will be seen that they do have the same general shape. Indeed, the agreement between $(I'_\nu)_2$ and the experimental curve is all that can be expected when account is taken of the approximate nature of the theory involved and of the fact that since the experimental curve is a derived curve, its shape can be varied within rather wide limits by smoothing the original data in different ways. It will be noticed that the best agreement between the theoretical and experimental curves is obtained if the potential assumed to correspond to the Duane-Hunt limit for the setting of the spectrometer used is reduced by about 0.6 ω -unit or by about 9 volts. This would make only an insignificant change in the value of $\frac{h}{e}$ obtained from this experiment; moreover, this change would be in such a direction as to increase rather than to decrease the discrepancy between the values of $\frac{h}{e}$ found in this way and in other

ways.

It may be said in conclusion that the effect of the extra-nuclear electrons in the atoms composing the target of an x-ray tube on the spectral distribution of energy in the radiation from that tube is not of such a nature as to remove the present discrepancy between the value of $\frac{h}{e}$ obtained from the measurement of x-ray isochromats and the value found from other experiments with the use of the Bohr formula for the Rydberg constant, but that it is able to account for the knee found by Du Mond and Bollman in the isochromat in the immediate vicinity of the Duane-Hunt limit. It should be said further that the theory in its present form leads one to expect that this knee will be present when targets of some substances are used and absent when targets of other substances are used, but it is not in a position to predict whether this knee will be present or not when a target of any given substance is used.



Theoretical "Derived Curves"
(See page 88)

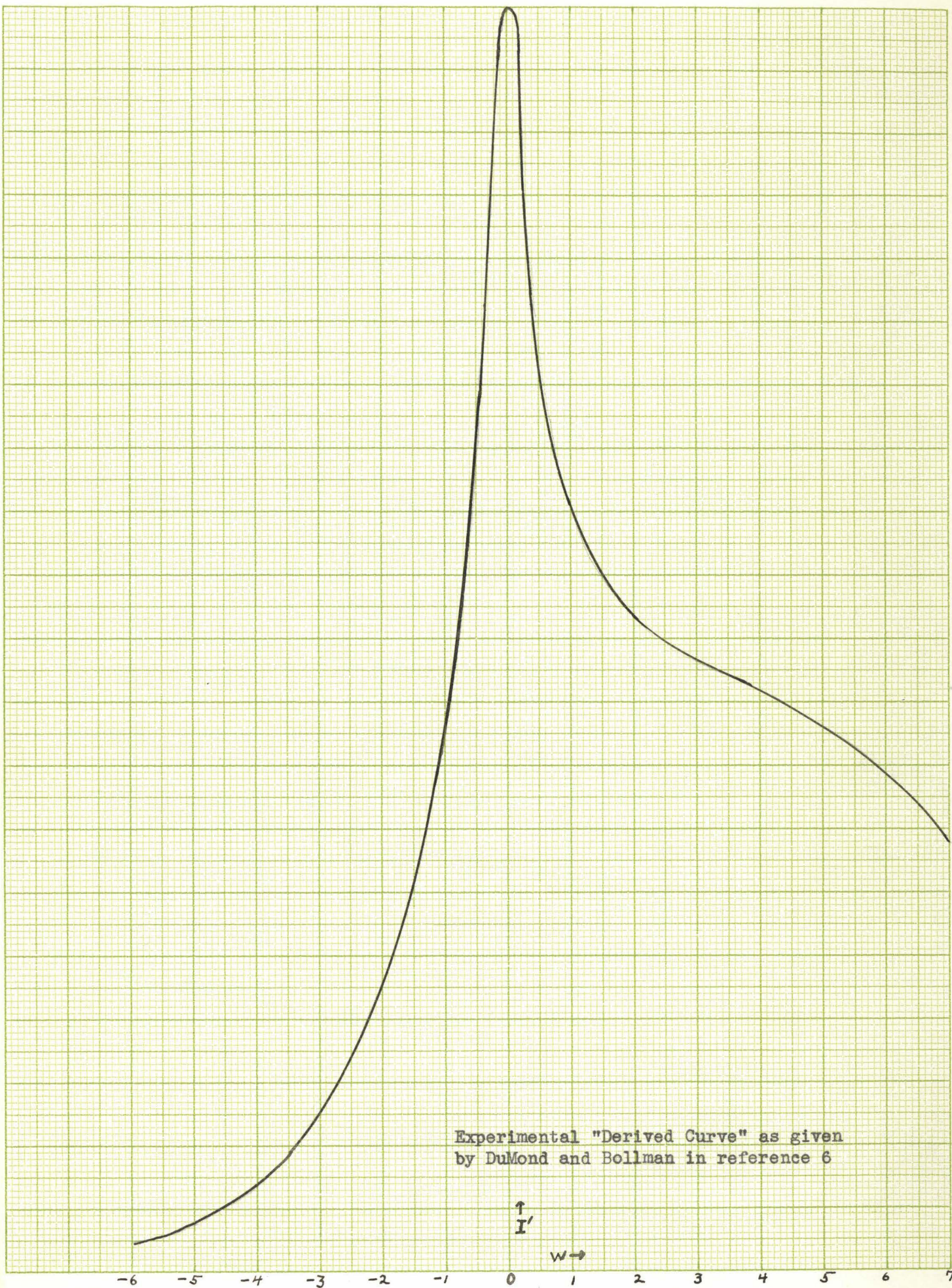
$(I'v)_2$

$(I'v)_1$

I'

$W \rightarrow$

-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7



Experimental "Derived Curve" as given
by DuMond and Bollman in reference 6

↑
 I'

$W \rightarrow$

-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7

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