Theory of the Dispersion and Absorption of Helium

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I. Herzfeld and Wolf were able to conclude from the behavior of the refractive index of helium in the visible spectrum that the continuous absorption of the gas below the 507A series limit plays an essential part in producing the observed refractivity. II. The present investigation involves a quantum mechanical calculation of the actual strength of this continuum, and also of the resonance line at 584A. As a by-product, the atomic absorption coefficient for x-rays is computed. III. The accuracy of the calculations is discussed. The 30 percent deviation from the present value of Vinti's value for the strength of the resonance line is accounted for. IV. The f sum rule is verified to 2 percent and the experimental refractive index is checked within 3 percent. V. It is discussed why the continuous spectrum is relatively so much stronger in helium than in hydrogen and the alkali metals.

I. INTRODUCTION

THE object of the present paper is to account for the refractive index of helium, as observed by C. and M. Cuthbertson,[1] by calculating the strengths f_i of the absorption frequencies ν_i appearing in the ordinary dispersion formula

$$n-1 = (Ne^2/2\pi m)\Sigma_i f_i/(\nu_i{}^2 - \nu^2). \qquad (1)$$

Here N is the number of atoms per cc, e and m are the electronic charge and mass, ν is the frequency of the incident light, and the ν_i are the absorption frequencies due to transitions from the ground state of the atom to higher energy levels. Even before any theory existed for the calculation of the f_i, Herzfeld and Wolf[2] were able to obtain some information as to their sizes and the position of the ν_i by considering only one or two terms of the infinite series (1), and adjusting the four disposable constants f_1, f_2, ν_1, ν_2, so as best to fit the experimental data. The absorption of helium is due to a line spectrum starting at 584A and running to a limit at 505A, and a continuous spectrum which starts at the series limit and extends to shorter wave-lengths. Their conclusion was that the contribution of the f's of the line spectrum is considerably outweighed by the effect of the f distributed over the continuous spectrum.

With quantum mechanics at his disposal, Vinti[3] has been able to compute approximate values for the f_i of the line spectrum of helium. The total effect of all the lines involving single electron jumps, he found, is at most 0.54; of all lines involving double jumps, at most 0.04. The f sum rule of Reiche, Kuhn, Thomas (see reference 11) says that the total electron number of helium is 2; thus Vinti could conclude that the integrated f of the continuous spectrum is at least 1.42. The accuracy of Vinti's work is discussed later (Section III). His most important contribution as far as the present work is concerned is the determination of an upper bound for the strength of double jumps.

In the following work double jumps are neglected, not only because they are weak, but also because their frequencies are so high that they contribute very little to the right side of Eq. (1). The error in the visible refractive index made by neglecting them is of the order of one percent or less. The number of excited states which need be considered is further reduced by the selection rules. Since the ground state of helium, $(1s)^2 {}^1S$, is even singlet with orbital quantum number $L=0$ and magnetic quantum number $m=0$, it can make dipole transitions only to odd singlet states for which $L=1 : {}^1P^0$. Further, according as the light is right or left handed circularly polarized or polarized parallel to the Z axis, the

[1] C. and M. Cuthbertson, Proc. Roy. Soc. **A135**, 40 (1932).

[2] K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **76**, 71, 567 (1925).

[3] J. P. Vinti, Phys. Rev. **42**, 632 (1932). This paper appeared when the present work was being prepared for publication.

magnetic quantum number m of the excited state must be ± 1 or 0. The only such states which can be reached by jumps of a single electron are of the type $(1s, np)$ $^1P^0$. Below, the f value of the resonance line transition to $(1s, 2p)$ $^1P^0$ is calculated, as well as the f values for the continuous spectrum of $^1P^0$ levels beyond the series limit.

II. CALCULATION OF ELECTRON NUMBERS

The electron number or strength, f, of the transition from the S state with wave function φ to the triply degenerate P state with wave functions $\psi_m (m = -1, 0, 1)$ can be determined from the equation[3a]

$$f = (8\pi^2 m\nu/3h)\Sigma_m\{\,|X_m|^2 + |Y_m|^2 + |Z_m|^2\}.$$

Here m is the electronic mass, $h\nu$ the energy $E_1 - E_0$ gained in the transition, and

$$Z_m = \int \varphi(z_1 + z_2)\psi_m dV \qquad (2)$$

is the matrix element of the z component of the total electronic displacement. In what follows, the unit of energy is Rh (Rydberg's constant: $R = 3.29 \times 10^{15}$/sec.), and the unit of distance is $h^2/16\pi^2 me^2$; that is, $a/4$, where $a = 0.528 \times 10^{-8}$ cm is the Bohr radius for hydrogen. As a conse-

quence of spherical symmetry and the choice of units,

$$f = Z_0^2(E_1 - E_0)/16. \qquad (3)$$

As wave function for the ground state, the eigenfunction of Hylleraas[4] is used, the most accurate known for any atom except hydrogen:

$$\varphi = (8\pi^2)^{-\frac{1}{2}}F = (8\pi^2)^{-\frac{1}{2}} \exp{(-kr_1 - kr_2)}$$
$$\times (A + Br_1 + Br_2 + Cr_1^2 + Dr_1r_2 + Cr_2^2$$
$$+ Er_1r_2 \cos\theta + Fr_{12}). \qquad (4)$$

Here r_1, r_2, and r_{12} are the distances of the two electrons from the nucleus and from each other, θ the angle between r_1 and r_2; $A = 0.1922$, $B = -0.00485$, $C = 0.00156$, $D = -0.00229$, $E = 0.00076$, $F = 0.0170$, $k = 0.455$; the corresponding value of the energy E is -1.8065, as against the experimental value -1.8070. φ is a pure radial function; that is, it depends upon the size and shape of the triangle r_1, r_2, r_{12}, but not upon the orientation of this triangle in space.

The wave functions ψ_m for a $^1P^0$ state depend also upon the orientation in space of the triangle of charges; but, as Breit[5] has shown, in analogy to the case of hydrogen this angular part of the helium wave function may be split off to give a wave equation involving the radial part G:

$$\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial G}{\partial r_1}\right) + \frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial G}{\partial r_2}\right) + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial G}{\partial\theta}\right) + \frac{2}{r_1^2}\left(\cot\theta\frac{\partial G}{\partial\theta} - G\right)$$

$$- \frac{2}{r_2^2\sin\theta}\frac{\partial PG}{\partial\theta} + \left(\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{2r_{12}} + \frac{E-4}{16}\right)G = 0. \qquad (5)$$

The permutation operator P above is defined by $PG(r_1, r_2, \theta) = G(r_2, r_1, \theta)$. G is to be normalized so that

$$\tfrac{2}{3}\int G(G + PG\cos\theta)r_1^2 r_2^2 \sin\theta dr_1 dr_2 d\theta = 1. \qquad (6)$$

The complete wave function ψ_0 is connected with G by the relation

$$\psi_0 = (8\pi^2)^{-\frac{1}{2}}[G\cos b$$
$$+ PG(\cos\theta\cos b - \sin\theta\sin b\cos c)]. \qquad (7)$$

The angles a, b, and c are the Euler angles used

to describe the orientation of the triangle in space: a describes rotation about the Z axis, b is the angle between the Z axis and the radius vector to the first electron, and c indicates rotation about this radius. Eq. (5) is exact for both the resonance and the continuous levels.

The wave function for the resonance level $(1s, 2p)$ $^1P^0$ may be determined by the simple variational method used by Breit[6] in another

[3a] See, for example, Born and Jordan, *Elementare Quantenmechanik*, 1st edition, p. 247.

[4] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929). Hylleraas' function, given in elliptical coordinates, is re-expressed above in terms of r_1, r_2, and θ, and has been normalized by use of his normalization integral.

[5] G. Breit, Phys. Rev. **35**, 569 (1930).

[6] G. Breit, Phys. Rev. **36**, 383 (1930).

connection. If the term $1/r_{12}$ were absent in Eq. (5), the radial function G would be $r_1 \exp(-r_1/4 - r_2/2)$. For the perturbed function a similar form is chosen, involving three adjustable constants, g, c, and a:

$$G(r_1, r_2, \theta) = h(gr_1 - c) \exp(-gar_1/2 - gr_2/2). \quad (8)$$

These constants are varied to make the value of the energy averaged over the state a minimum. The result is: $g = 1.00$, $c = 0.238$, $a = 0.25$; the normalization factor $h = 0.00397$; and the average value of the energy is -0.2447, as compared with the experimental value -0.2476 (measured in units Rh above ionization).

The wave functions for the continuum of energy levels beyond the series limit also satisfy Eq. (5), which is exact. An approximation for an excited function is secured by taking one electron (2) as bound in a $1s$ state acted upon only by the charge $2e$ of the nucleus, and the other electron (1) free (i.e., in a p hyperbolic orbit) and acted upon by a centralized charge of $2e - e = e$. The effect of this approximation is to replace the term $(1/r_1 - 1/2r_{12})$ in Eq. (5) by the term $1/2r_1$, the difference between the two falling off for large r_1 as r_2/r_1^2. The solution of the altered wave equation is the product of functions of r_1 and r_2 alone:

$$G(r_1, r_2, \theta) = N(E) \exp(-r_2/2) \oint \exp(ir_1z/4)(z + E^{\frac{1}{2}})^{1 + iE^{-\frac{1}{2}}}(z - E^{\frac{1}{2}})^{1 - iE^{-\frac{1}{2}}} dz. \quad (9)$$

E is the energy above ionization. The representation of the function of r_1 through a complex integral, as well as the determination of the normalization factor

$$N(E) = 3^{\frac{1}{2}}(512\pi)^{-1}(1 + E)^{-\frac{1}{2}}(1 - e^{-2\pi E^{-\frac{1}{2}}})^{-\frac{1}{2}} \quad (10)$$

are carried out by the methods of Schrödinger[7] and Fues.[8] The function of r_1 must be defined by a complex integral or an infinite series because it cannot be expressed in finite terms through known (i.e., tabulated) functions. In the integration, z runs around a circle surrounding the two branch points $-E^{\frac{1}{2}}$ and $E^{\frac{1}{2}}$. It should be stated at this point that it is impossible in the continuous spectrum to normalize G so that $\int \psi_0^2(E) \times dV = 1$, because the probability of the free electron being at infinity is not zero. Instead, $N(E)$ is chosen (following Fues) so that

$$\int \psi_0(E) \int_{E - \Delta E}^{E + \Delta E} \psi_0(E') dE' dV = 1,$$

where ΔE is arbitrarily small. It is a consequence of this changed normalization that Eq. (3) gives for the continuous spectrum, not f, but df/dE.

Since the main part of the electron number of helium lies in the continuum, it is important to know how good is the approximate function given by Eq. (9). That function represents the outer electron moving in the field created by a

charge of e at the nucleus; but is clear that when r_1 is small compared with the radius of the $1s$ orbit, the effective charge acting on the free electron will have increased to nearly $2e$. If it is assumed that the free electron does not influence the charge distribution of the $1s$ electron, the potential field $V(r_1)$ in which the free electron moves may be calculated:

$$r_1 V(r_1) = -\tfrac{1}{2} - \tfrac{1}{2}(1 + r_1 + \tfrac{1}{2}r_1^2) \exp(-r_1).$$

The effective charge $Z_{eff.} = -2r_1 V(r_1)$ is plotted in Fig. 1. The wave function for the free electron in this field of force may be found by numerical integration of the corresponding one-electron Schrödinger equation. The solution for $E = 0.01$, multiplied by the radial density factor r_1, is shown by the curve He* in Fig. 1; and the corresponding solution for the original potential field $r_1 V(r_1) = -\tfrac{1}{2}$ is shown by the curve marked H*, which is the exact wave function for hydrogen for $E = 0.01$. The normalization of the two curves is the same. For large values of r_1, the excited functions behave nearly as $\sin(E^{\frac{1}{2}}r + p)$. It is seen that the main effect of the change in field is to pull the waves in towards the nucleus. Curve He in Fig. 1 represents a sort of effective wave function for the ground state of helium, such that the matrix element Z_0 of the electron displacement is given by $\int \text{He } r_1 \text{ He*} dr_1$, the integration over r_2 and θ having been performed. For the given value 0.01 of E, the electric moment calculated on the basis of the modified field

[7] E. Schrödinger, Ann. d. Physik **80**, 437 (1926).
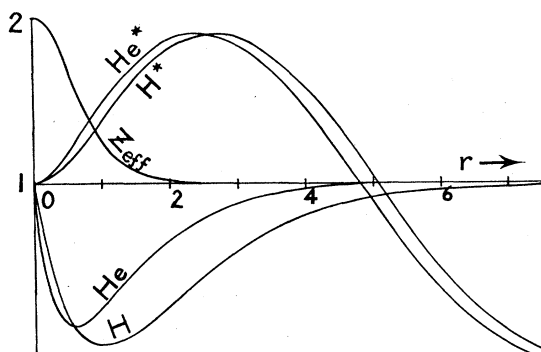
[8] E. Fues, Ann. d. Physik **81**, 281 (1926).

FIG. 1. $Z_{eff.}$, effective charge acting on excited electron of helium. H* and He*, excited wave functions of hydrogen and helium for $E=0.01$. H, ground function of hydrogen; He, "effective" ground function of helium (cf. Section II). r is in units of the Bohr radius. Functions are not normalized.

is about 5 percent greater than that calculated from the original field. Consideration of the free-electron wave equation shows that for large values of E the effect of the field change on the excited wave function will grow progressively less. Of course, the above discussion considers

only the effect of the inner electron on the motion of the outer; but because this effect is so small, it may be considered that the converse effect will also be small. Accordingly, hydrogenic wave functions are used in the following calculations for the continuous spectrum.

The necessary eigenfunctions being known, the matrix element Z_0 may be calculated. As in the case of hydrogen, the whole integration reduces to a radial integral:

$$Z_0 = \tfrac{2}{3} \int \int \int F(r_1, r_2, \theta)(r_1 + r_2 \cos \theta)$$
$$\times G(r_1, r_2, \theta) r_1{}^2 r_2{}^2 \sin \theta dr_1 dr_2 d\theta. \quad (11)$$

For the resonance line, Z_0 is found to be 1.65; since $E_1 - E_0 = -0.247 + 1.807 = 1.56$, Eq. (3) gives 0.266 for the f value of the resonance line.

For the continuous spectrum, $E_1 - E_0 = 1.807 + E$. $Z_0(E)$ is found by integrating (11) first over θ, r_2, and r_1; then the integration with respect to the complex quantity z involved in G (Eq. (9)) may be carried out by the method of residues. The result is:

$$df/dE = Z_0{}^2(E)(1.807+E)/16 = (1.807+E)(1+E)^{-1}(1-e^{-2\pi E^{-\frac{1}{2}}})^{-1}[(E+3.31)^{-5}(0.227E^5$$
$$+3.76E^4+66.3E^3+389E^2+1250E+943) \exp (-2E^{-\frac{1}{2}} \arctan (E^{\frac{1}{2}}/1.82)) - (E+31.8)^{-3}$$
$$\times (0.227E^3+19.9E^2+535E+3280) \exp (-2E^{-\frac{1}{2}} \arctan (E^{\frac{1}{2}}/5.64))]^2. \quad (12)$$

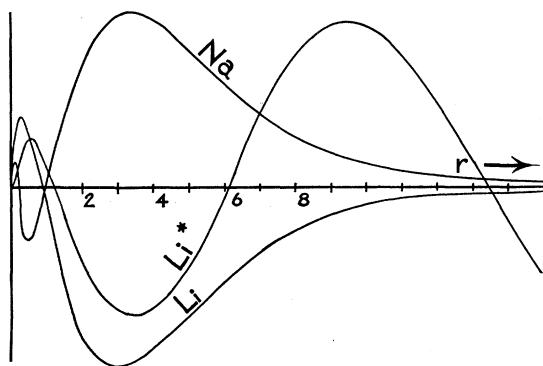Values of df/dE calculated from this formula for several values of E are given in Table I. The

FIG. 2. Wave functions for the alkali metals, not normalized. Li and Na are ground functions; Li* is excited function for $E=0$. r in Bohr units. (Curves taken from B. Trumpy.)*

* B. Trumpy, Zeits. f. Physik 71, 728 (1931), and 61, 54 (1930).

variation of the electron number with the energy E of the excited level may be seen from Fig. 3, where there is plotted against the wave-length λ in A $(\lambda=911(1.807+E)^{-1})$ the closely related quantity α, the coefficient of linear absorption appearing in the ordinary intensity formula
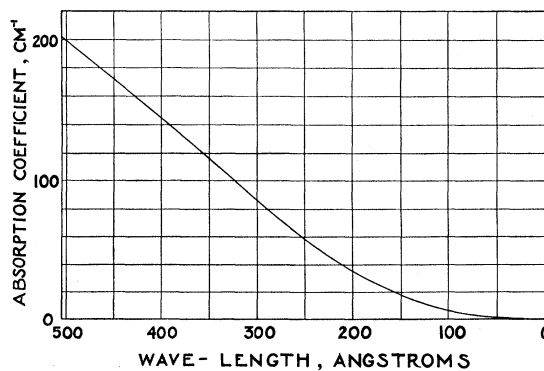

FIG. 3. Theoretical curve for the absorption coefficient of helium. (Cf. Section II.)

TABLE I. *Electron number of helium.*
E is in units Rh.

E	df/dE	E	df/dE
0.0	0.93	3.0	0.146
0.2	0.81	3.5	0.116
0.4	0.70	4.0	0.093
0.6	0.62	5.0	0.065
0.8	0.53	6.0	0.046
1.0	0.47	7.0	0.033
1.3	0.38	8.0	0.026
1.6	0.31	9.0	0.020
2.0	0.25	10.0	0.015
2.5	0.19	16.0	0.0056

Total f, continuum: 1.58. f value, resonance line: 0.266.

$I = I_0 \exp(-\alpha x)$. In terms of f, at standard pressure and temperature,

$$\alpha = \pi N e^2 / (mc) df/d\nu = \pi N e^2 / (mcR) df/dE$$

$$= 207 (df/dE) \ (cm^{-1}).$$

The only experiments made so far upon the strength of the continuous absorption of helium are not quantitative enough to compare with Fig. 3.[9]

The behavior of the electron number for large values of E may be found by expanding the exponentials in Eq. (12). For very short wavelengths, $df/dE \sim 2.8 \times 10^{-8} \lambda^{3.5}$; consequently the "true" absorption coefficient τ_a for x-rays, per atom, is $2 \times 10^{-25} \lambda^{3.5}$. This formula cannot be expected to hold for wave-lengths less than, say, 5A, because above no account is taken of the difference in the phase of the incident radiation over the atom.

III. ACCURACY OF CALCULATIONS

The accuracy of the continuous wave functions has been discussed above. For $E = 0.01$ the inaccuracy in the calculated value of the electron number is of the order of 10 percent, and decreases for increasing values of E.

The inaccuracies in the ground and excited function show up doubled in the electron number. Eckart[10] has shown that the error in a wave function obtained by variational means is of the order of $(\Delta E/(E_1 - E_0))^{\frac{1}{2}}$. ΔE is the difference be-

tween the computed and correct energy values, and $E_1 - E_0$ is the distance to the next higher energy level of the same spectral type. For the ground function (Eq. (4)), $E_1 - E_0$ is 1.52 and ΔE is 0.00052, giving a percentage error of the order of two. For the resonance level wave function (Eq. (8)), $E_1 - E_0$ is 0.137 and ΔE is 0.003, implying a percent inaccuracy of the order of 15. Thus the maximum error in the computed electron number $f = 0.266$ of the resonance line is of the order of 30 percent. However, Vinti[3] obtains an f value of 0.349, 31 percent higher. It is probable that the difference between the two values arises mainly from the ground function which he uses; it gives an energy error ΔE of 0.052, implying a percent error of possibly 18 in the ground function, and a possible error of 60 percent in the electron number, since his resonance wave function has practically the same accuracy as the one used above.

IV. THE f-SUM RULE AND REFRACTIVE INDEX

The sum rule of Reiche, Kuhn and Thomas[11] demands that the total electron number of helium be 2. From formula (12) the contribution of the continuum to f was found to be 1.58. For the resonance level $f = 0.266$. The strength of the other lines in the same spectral series $(1s, np)$ $^1P^0$ may be estimated from the formula valid asymptotically for large n : $f_n \alpha 1/n^3$.[12] This gives as the contribution of the rest of the series 0.266

$$\times 2^3 \times \sum_{n=3}^{\infty} 1/n^3 = 0.159.$$ Summing up, the total f is

$1.58 + 0.266 + 0.159 = 2.00$. This is slightly too large, for Vinti estimates that double jumps contribute of the order of 0.04 to f.

The electron number being known, the refractive index can be calculated from Eq. (1), and compared with experiment. Frequencies lying in the visible spectrum are so small compared with the absorption frequencies that the structure of the latter does not show up; this is why Cuthbertson can represent his measurements by means of a one term formula:

$$n - 1 = 1.32614 \times 10^{27} / (3.83137 \times 10^{31} - \nu^2). \quad (13)$$

The mean or effective absorption frequency in

[9] See, for example, C. Cuthbertson, Proc. Roy. Soc. A114, 650 (1927).

[10] C. Eckart, Phys. Rev. 36, 878 (1930).

[11] W. Kuhn, Zeits. f. Physik 33, 408 (1925).

[12] Hartree, Proc. Camb. Phil. Soc. 25, 75 (1929).

this formula lies at 485A. To simplify comparison of theory with experiment, choose the constants A and F in the equation

$$n-1 = (Ne^2/2\pi m)A/(R^2F^2-\nu^2)$$

so that at some convenient frequency Re, lying in the midst of Cuthbertson's observations, this one term approximate formula has the same ordinate and slope as the right-hand side of Eq. (1). Take $e = 0.25$, corresponding to 3644A. F and A are given by $F^2-e^2 = I/J$; $A = I^2/J$; here

$$I = \int \frac{df(E)}{(E-E_0)^2-e^2}; \quad J = \int \frac{df(E)}{((E-E_0)^2-e^2)^2}.$$

(This Stieltjes integral cares for both line and continuous spectrum). The f values calculated above for the continuum and the resonance line, together with the values derived for the series $(1s, np)^1P^0$ by means of the $1/n^3$ law give for A, the effective electron number, 1.27; and for F, the effective frequency, 1.89, corresponding to 482A. The corresponding one term formula is

$$n-1 = 1.38 \times 10^{27}/(3.865 \times 10^{31} - \epsilon^2). \quad (14)$$

There is 3 percent difference between this formula and Cuthbertson's (Eq. (13)).

V. DISCUSSION

There are two independent checks on any calculation of f values: the f sum rule and the experimental refractive index. The fact that one criterion is fulfilled to 2 percent and the other to 3 percent makes it possible to conclude that the actual error in the electron number calculations is much less than the possible error indicated in Section III, and that the refractive index of helium is satisfactorily accounted for by theory.

The question arises as to why the continuous spectrum of helium is so much stronger than that of the hydrogen-like elements (cf. Table II). The strength of the absorption varies as the square of the matrix element of the electric moment. To give an indication why this matrix

TABLE II. *Strength of ultraviolet absorption.*

Atom	Total f of continuum	df/dE, series limit	Reference
H	0.437	0.78	Suguira[13]
He	1.58	0.93	Present paper
Li	0.24	0.46	Trumpy[14]
Na	0.0021	0.038	Trumpy[15]
K		0.0024	Phillips[16]

element is larger for helium than for other atoms, the ground and excited wave functions of several atoms are shown (unnormalized) in Figs. 1 and 2, each multiplied by the density factor r. To obtain the matrix element, the factor r must be used again: $Z = \int ArA^*dV$, for an atom A. The immediate neighborhood of the nucleus contributes very little to this integral; and the essential part of the excited function varies only slightly from atom to atom. The important variation occurs in the ground function. The maxima of all the curves occur at larger values of r than the maximum of the helium ground function; and this shift to larger values of r is such that an important interference effect takes place in the formation of the matrix element integral except in the case of helium. That is to say, the integrand oscillates above and below zero with increasing r because of the excited function; this oscillation has died out with helium at the first half wave; but with hydrogen, and more especially with sodium and lithium, the oscillation falls off more slowly, and the positive and negative parts of the integrand to a considerable extent annul one another. Thus the essential factor is the relation between the wave-length of the free electron and the radius of the atom.

The author is indebted to Professor Herzfeld for suggesting the foregoing problem, and is very grateful to him for the advice received in working it out.

[13] Sugiura, J. de Physique **8**, 113 (1927).
[14] B. Trumpy, Zeits. f. Physik **54**, 373 (1929).
[15] B. Trumpy, Zeits. f. Physik **71**, 720 (1931).
[16] M. Phillips, Phys. Rev. **39**, 905 (1932).