# Anomalous Dispersion and Scattering of X-Rays*

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(Received January 25, 1954)

The theoretical expressions for the anomalous dispersion of x-rays have been integrated for any positive value of $p_q$ in a $C_q\lambda^{p_q}$ term in the distribution of "dispersion" oscillators for the $q$ shell of electrons. This distribution may be written generally as the sum of $n$ terms of the form $C_{qn}\lambda^{p_{qn}}$ or, as is commonly done, as a single term. Damping has been retained, its effect evaluated and shown to be negligible except for $\lambda$ extremely close to the wavelength of an absorption discontinuity. With damping neglected, universal dispersion curves are presented. If $p_q$ and $g_q$ (the oscillator strength) are known, the anomalous part of the refractive index or of the atomic scattering factor can be readily deduced from the universal curves.

Comparison of the more exact theoretical values with experiment shows less satisfactory agreement than before.

## INTRODUCTION

IN comparing theoretical predictions with experimental measurements of refractive index $r$ for x-rays,

$$r = 1 - (\delta + i\beta),$$

and for the atomic scattering factor $f$, written for very small scattering angle as

$$f = (1/A\lambda^2)(\delta^2 + \beta^2)^{\frac{1}{2}},$$

where $A$ is a constant, it has become the custom to assume that the frequency distribution of the theoretical "dispersion" oscillators follows a $\lambda^3$ relation, where $\lambda$ is the wavelength.[1] This assumption makes for easy integration of the expression for $\delta$ (or for $f$), but it is not in accord with x-ray absorption measurements: In general, $\lambda^{11/4}$ is probably better for the photoelectric absorption by $K$ electrons, $\lambda^{7/3}$ by $L$ electrons,[2,3] and perhaps $\lambda^{5/2}$ by $M$ electrons.[4] The exponent for a given electron shell

varies with atomic number. Needless to say, the numerical value of the exponent is important in the region of anomalous dispersion.

As an additional complication, the exponent may vary with wavelength. Hönl[5] used a two-term expression for $K$ electrons, viz., $C_K(\lambda/\lambda_K)^3 + D_K(\lambda/\lambda_K)^4$, where $C_K = 4/3$ and $D_K = -1/3$; this is equivalent to a single term with exponent $p_K(\lambda)$, such that $p_K = 2.67$ at $\lambda_K$, 2.78 at $\lambda_K/2$, and 2.94 at $\lambda_K/200$. Hall[4] also discussed this expression. Victoreen[2] concluded that it expresses well the experimental data for the net effect of all the electron shells; the $C/D$ ratio depends markedly upon the atomic number and upon the wavelength region (i.e., $\lambda < \lambda_K$ or $\lambda_K < \lambda < \lambda_L$). However, careful analysis of the available experimental data for the $K$ electrons of copper, for example, indicates that $p_K$ is very nearly 2.75 and does not vary significantly in the range 0.1A $< \lambda < \lambda_K$. With more extensive and accurate absorption measurements, it may well be necessary to use two (or more) terms in the general sum $\sum_n C_{qn}\lambda^{p_{qn}}$. In any case, the general integration must be carried out separately for each term.

In the present paper, the dispersion expression is integrated for a general $\lambda^{p_q}$ term, where $p_q$ may be any number greater than zero. Combinations of such terms may be made when and if desired. Typical calculations are shown for $p = 2$, 7/3, 5/2, 11/4, 3, and 4. The necessity of including the anomalous effects of more than one shell of electrons is pointed out[6] with the correlative conclusion that there is practically no region of "normal" x-ray dispersion.

It has also become the custom to neglect the damping factor. In the present integrations and calculations, damping has been retained so as to allow evaluation of the error made in any specific case due to neglect of

[1] For example, see R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, Ltd., London, 1948); and A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935). W. Heitler [*The Quantum Theory of Radiation* (Oxford University Press, London, 1944), second edition, pp. 129–137] discusses "dispersion" oscillators quantum mechanically in terms of matrix elements of transitions of the inner electron to the various bound and unbound states. This discussion includes "oscillator strength" as introduced later.

[2] K. Grosskurth, Ann. Physik **20**, 197 (1934); S. J. M. Allen, Phys. Rev. **28**, 907 (1926); Compton and Allison, reference 1; A. Jönsson, *Inaugural Dissertation* (Upsala University, Upsala, 1928); and J. Victoreen, J. Appl. Phys. **19**, 855 (1948) and **20**, 1141 (1949). These measurements refer to all types of electrons; appropriate subtractions are necessary to deduce the exponent of $\lambda$ for a particular electron shell. (Subtraction must first be made for the scattering part of the measured absorption.)

[3] With damping terms neglected, the integration for $\delta$ or $f$ has been done for $\lambda^{5/2}$ by E. J. Williams, Proc. Roy. Soc. (London) **A143**, 358 (1934). Williams, and also J. A. Bearden and C. H. Shaw [Phys. Rev. **46**, 759 (1934)] have interpolated between $\lambda^{5/2}$ and $\lambda^3$ for $\lambda^{11/4}$.

[4] No direct measurements of $p$ in $\lambda^p$ for $n$ electrons are known. However, $p_{LI}$ is smaller than $p_{LII,III}$, and it is the behavior of the $L_I$-electrons that causes $p_L$ to be so small. Similar behavior is observed for the $M_I$-electrons relative to the other $M$ electrons. See H. Robinson, Proc. Roy. Soc. (London) **A104**, 455 (1923); and H. Hall, Revs. Modern Phys. **8**, 358 (1936), and references.

[5] H. Hönl, Ann. Physik **18**, 625 (1933) and Z. Physik **84**, 1 (1933). Hönl's treatment is based on theoretical assumptions that are known to be not valid in the present range of x-ray energies. (*Note added in proof.*—H. Eisenlohr and G. L. J. Müller [Z. Physik **136**, 491 and 511 (1954)] have recently extended Hönl's treatment to $L$ electrons).

[6] The authors note, after completion of the present work, that this point has also recently been made by H. Eisenlohr and G. L. Müller, Z. Naturforsch. **8a**, 429 (1953).

damping. It turns out that neglect of damping is well justified except in the case of $\lambda$ extremely close to $\lambda_q$, the wavelength of an absorption discontinuity; and for this narrow region the difference between $\lambda$ and $\lambda_q$ has, as yet, very little practical meaning. With damping neglected, universal curves for anomalous dispersion are useful and convenient.

Comparison of the present calculations with experiment show less good agreement than before.

## EXPRESSION FOR $\delta$ OR $f$

### The Integral

According to quantum-mechanical dispersion theory,[1] the refractive index, in terms of various electron shells $q$, is

$$r = 1 - (\delta + i\beta) = 1 - A\lambda^2 \sum_q \int_{\omega_q}^{\infty} \frac{\omega^2 (dg/d\omega_v)_q}{\omega^2 - \omega_v^2 - i\eta_q\omega} d\omega_v. \quad (1)$$

The real unit decrement and the imaginary terms are

$$\delta = \sum_q \delta_q = A\lambda^2 \sum_q \int_{\omega_q}^{\infty} \frac{\omega^2 (\omega_v^2 - \omega^2)(dg/d\omega_v)_q}{(\omega^2 - \omega_v^2)^2 + \eta_q^2\omega^2} d\omega_v, \quad (2)$$

$$\beta = \sum_q \beta_q = A\lambda^2 \sum_q \int_{\omega_q}^{\infty} \frac{\eta_q\omega^3 (dg/d\omega_v)_q}{(\omega^2 - \omega_v^2)^2 + \eta_q^2\omega^2} d\omega_v, \quad (3)$$

where

$$A = \frac{Ne^2}{2\pi m_e c^2} \frac{\rho}{M} = 2.7019 \times 10^{10} \frac{\rho}{M},$$

and $e$ = electronic charge, $N$ = Avogadro's number, $m_e$ = electronic mass, $c$ = velocity of light, $\rho$ = density, $M$ = molecular weight, $\omega = 2\pi\nu$, $\nu$ = incident x-ray frequency; $\omega_v = 2\pi\nu_v$, $\nu_v$ = frequency of dispersion oscillator, $\omega_q = 2\pi\nu_q$, $\nu_q$ = frequency of the $q$-absorption discontinuity; $(dg/d\omega_v)_q$ = oscillator density of $q$-type electrons near $\omega_v$; and $\eta_q$ = damping factor. Although the oscillators extend in frequency from 0 to $\infty$, the only ones actually operating are those[7] from $\omega_q$ to $\infty$. The quantity $(\delta + i\beta)$ is positive; the minus sign in Eq. (1) indicates that the phase of the scattered waves is opposite to the phase of the incident wave. The imaginary term, $i\beta$, represents a wave $\pi/2$ out of phase, and is an absorptive term. This wave has a negligible effect in angular deviations of the beam, but has a significant role in scattered intensity in the anomalous region, especially at small scattering angles.[1] The integral of Eq. (3) for $\beta$ is easy to evaluate and is discussed later. The essential problem is $\delta$.

The operating oscillators involve the photoelectric absorption process, and the oscillator density can be written

$$(dg/d\omega_v)_q = (m_e c/2\pi^2 e^2)\mu(\omega_v)_q, \quad (4)$$

where $\mu(\omega_v)_q$ is the atomic photoelectric absorption coefficient of $q$-type electrons for frequency $\omega_v$. For convenience we shall write the absorption coefficient as following a single term in the sum $\sum_n C_{qn}\lambda^{p_{qn}}$, then

$$\mu(\omega_v)_q = (\omega_v/\omega_q)^{-p_q}\mu_q \quad \text{for } \omega_v > \omega_q,$$
$$= 0 \quad \text{for } \omega_v < \omega_q, \quad (5)$$

where $\mu_q$ is the coefficient for $\omega_v = \omega_q$. With Eqs. (4) and (5) placed in (1), we may write

$$\delta = \sum_q \delta_q = A\lambda^2 \sum_q g_q \operatorname{Re}(J_q), \quad (6)$$

where $J_q$, containing the integral to be evaluated, is

$$[J_q]_p \equiv 2\alpha x^2 \omega_q^{p_q+1} \int_{\omega_q}^{\infty} \frac{\omega_v^{-p_q}}{\omega^2 - \omega_v^2 - i\eta_q\omega} d\omega_v. \quad (7)$$

The quantities $\alpha$ and $x$ are defined explicitly below. If the absorption coefficient is expressed as a sum, as discussed in the Introduction, Eq. (6) becomes

$$\delta = A\lambda^2 \sum_q g_q[\sum_n C_{qn} \operatorname{Re}(J_q)_{pn}] \quad (6a)$$

and Eqs. (5), (8), (16) and (18) must be similarly modified.

The oscillator strength $g_q$ in Eq. (6) may be obtained from an integration of Eq. (4), in which Eq. (5) has been inserted, viz.,

$$g_q = \int_{\omega_q}^{\infty} \left(\frac{dg}{d\omega_v}\right)_q d\omega_v = \frac{m_e c}{2\pi^2 e^2} \frac{\omega_q}{p_q - 1}\mu_q, \quad (8)$$

or $g_q$ may be obtained by some other method.[5,8]

### Evaluation of the Integral

The following relations are convenient:

$$x \equiv \omega/\omega_q, \quad y \equiv (\omega_q/\omega_v)^2, \quad z \equiv \frac{1 + i\zeta}{x^2(1 + \zeta^2)},$$
$$0 < \alpha \equiv n/m \equiv \tfrac{1}{2}(p_q - 1) < 1,$$
$$\zeta \equiv \eta_q/\omega, \quad (9)$$
$$a \equiv |z|^{1/m} \equiv 1/b,$$
$$\theta \equiv \tan^{-1}\zeta,$$
$$\gamma \equiv \exp(2\pi i/m).$$

Equation (7) becomes

$$[J_q]_p = \alpha z x^2 \int_0^1 \frac{y^\alpha}{y - z} dy, \quad (10)$$

and this can be evaluated by contour integration.

[7] For $\omega$ very close to $\omega_q$, we must be careful of the value we choose for $\omega_q$. Fine structure is observed in the experimental absorption coefficient in this region, structure composed of "resonance absorption lines" [of the sort reported by L. G. Parratt, Phys. Rev. **56**, 295 (1939); J. Trischka, Phys. Rev. **67**, 318 (1945), and by Y. Cauchois and N. F. Mott, Phil. Mag. **40**, 1260 (1949)]. Transitions to unfilled outer levels in the atom (or "bands" in the solid) are properly included in the integral. It has become the custom arbitrarily to take as $\omega_q$ the frequency at the first inflection point in the absorption curve, whereas a point about midway up the absorption discontinuity is probably more realistic for use in the dispersion equations.

[8] E. J. Williams, reference 3, and J. A. Wheeler and J. A. Bearden, Phys. Rev. **46**, 755 (1934).

## Case I

$|z| \leqslant 1$, i.e., $x \geqslant 1/(1+\zeta^2)^{\frac{1}{2}}$. ($|z|$ is the modulus of the complex $z$).

$$[J_q]_p{}^{\mathrm{I}} = zx^2\left[1 - \frac{\pi\alpha z^\alpha \gamma^{-n/2}}{\sin\pi\alpha} - \alpha\sum_{j=1}^{\infty}\frac{z^j}{(j-\alpha)}\right]. \quad (11)$$

The sum from $j=1$ to $\infty$ is easily evaluated to about 1 part in $10^5$ by taking no more than 7 terms when $|z| \lesssim \frac{1}{4}$.

For $|z|$ near unity, the number of necessary terms in Eq. (11) becomes impractically large, and we need a closed form expression. When $\alpha$ is rational, i.e., when $n$ and $m$ are integers, the closed form is

$$\left[\sum_{j=1}^{\infty}\frac{z^j}{(j-\alpha)}\right]^{\mathrm{I}} = -z^\alpha\sum_{k=0}^{m-1}\gamma^{kn}\ln(1-\gamma^k z^{1/m}). \quad (12)$$

## Case II

$|z| \geqslant 1$, i.e., $x \leqslant 1/(1+\zeta^2)^{\frac{1}{2}}$,

$$[J_q]_p{}^{\mathrm{II}} = zx^2\left[1 - \alpha\sum_{j=0}^{\infty}\frac{1}{z^j(j+\alpha)}\right], \quad (13)$$

and the closed form of the sum of Eq. (13), with $n$ and $m$ integers, is

$$\left[\sum_{j=0}^{\infty}\frac{1}{z^j(j+\alpha)}\right]^{\mathrm{II}} = -z^\alpha\sum_{k=0}^{m-1}\gamma^{k(m-n)}\ln(1-\gamma^k z^{-1/m}). \quad (14)$$

Equations (12) and (14) restrict $\alpha$ to the range $0 < \alpha < 1$, i.e., $1 < p < 3$. Theory (with hydrogenic wavefunctions) predicts $p > 3$ for $\omega \gg \omega_q$ (see Hall, reference 4), and some advantage may accrue from use of the two-term absorption expression $C_q\lambda^3 + D_q\lambda^4$ discussed in the Introduction. For $\alpha \geqslant 1$, but for case I, $\alpha$ cannot be an integer, the open sums must be put into the form

$$\sum_{j=1}^{\infty}\frac{T^j}{j-\epsilon} = -T^\epsilon\sum_{k=0}^{m-1}\sigma^{kn}\ln(1-\sigma^k T^{1/m}), \quad (15)$$

where $0 < \epsilon \equiv n/m < 1$, and $\sigma \equiv \exp(-2\pi i/m)$, by separating the appropriate terms and adjusting the index of summation. For $\alpha$ an integer, integration of Eq. (10) is straightforward: The change of variable $u=y-z$ produces an elementary integral always containing as one term $\int_{-z}^{} 1^{-z}u^{-1}du$. Since the path of integration is well defined, there is no question about the argument of the resulting logarithm.

Our final expression for $\delta$ for a medium containing different atomic species $s$ becomes

$$\delta = \sum_s A_s\lambda^2\{Z_s + \sum_q g_q[\mathrm{Re}(J_q)-1]\}, \quad (16)$$

where the real part of Eq. (11) or (13), in either open or closed form, is used for $\mathrm{Re}(J_q)$. The $q$ summation of $g_q$ gives the atomic number $Z$ by the so-called sum rule;[9]

[9] W. Kuhn, Z. Physik 33, 408 (1925), and F. Reiche and W. Thomas, Z. Physik 34, 510 (1925).

the use of this rule here minimizes calculational errors due to uncertainties in the $g_q$ values, and conveniently separates the normal and anomalous dispersion parts. The $\sum_s A_s\lambda^2 Z_s$ term is the normal dispersion term;[10] the $\sum_q$ terms are the anomalous contributions.

The expression for the modulus of the complex atomic scattering factor is

$$f = \sum_s[f_{1s}{}^2 + f_{2s}{}^2]^{\frac{1}{2}}, \quad (17)$$

where, for a single atomic species,

$$f_1 \equiv f_0 + \sum_q g_q[\mathrm{Re}(J_q)-1], \quad f_2 \equiv \beta/(A\lambda^2), \quad (18)$$

and $f_0$ is the "normal" (i.e., $\omega$ not near $\omega_q$) atomic scattering factor ($=Z$ if the scattering angle is zero as is assumed for $\delta$). Equation (17) neglects quadrupole and octopole oscillators; this neglect is justified unless the incident wavelength is small compared with the radius of the Bohr orbit $B_q$. Quadrupole oscillators cause an increase in $f_1$ of the order of $(2\pi B_q/\lambda)^2 \sum_q g_q[\mathrm{Re}(J_q)-1]$ and this increase depends, as does also $f_0$, upon the scattering angle.[5]

The expression for $f_2$ requires evaluation of $\beta$. The integration of Eq. (3) is readily carried out since (a) only those dispersion oscillators respond appreciably whose frequencies are very close to the incident frequency, i.e., $\omega_v$ need be distinguished from $\omega$ only in their difference, and (b) the variation in the oscillator density is negligible in this restricted range of frequencies. Then,

$$\beta_q = \frac{\omega}{2}A\lambda^2\left(\frac{dg}{d\omega_v}\right)_q \cot^{-1}\left(\frac{2(1-x)}{\zeta}\right),$$

and, by use of Eq. (4),

$$\beta = \sum_q \beta_q = \frac{c}{2\pi\omega}\frac{N\rho}{M}\sum_q \mu(\omega)_q\cot^{-1}\left(\frac{2(1-x)}{\zeta}\right). \quad (19)$$

When $x$ is appreciably greater or less than unity, the $\cot^{-1}$ term is $\pi$ or zero for the $q$-type electrons, and $\beta = \lambda\mu_l/4\pi$ where $\mu_l$,

$$\mu_l = (N\rho/M)\sum_q \mu(\omega)_q, \quad (20)$$

is the linear photoelectric absorption coefficient.

A more accurate method for evaluating $\beta$ is to gather the imaginary terms in the expression for $J_q$. This method is usually unnecessarily cumbersome; however, it has been carried out in the case of $p=2.5$. If $\zeta$ terms are neglected compared with $\pi$, the value of $\beta$ so obtained agrees with Eq. (18) except that now the $\cot^{-1}$ argument is $4(1-x^{\frac{1}{2}})/\zeta$ for $x \geqslant 1/(1+\zeta^2)^{\frac{1}{2}}$ and $4(1-x^{\frac{1}{2}})/x^{\frac{1}{2}}\zeta$ for $x < 1/(1+\zeta^2)^{\frac{1}{2}}$.

## DAMPING FACTOR

There has been some ambiguity as to the proper value of $\eta_q$ for use in the above expressions. Radiation damping of a dispersion oscillator predicts $\eta_0 = 2e^2\omega^2/3m_ec^3$. This

[10] Confirmation of the theory for the normal dispersion term is beautifully demonstrated by Bearden and Shaw, reference 3, and by J. A. Bearden, Phys. Rev. 54, 698 (1938).

TABLE I. Universal values of Re($J_q-1$).

| λ/λ_q | p=2.0 | p=7/3 | p=5/2 | p=11/4 | p=3 | p=4 |
|---|---|---|---|---|---|---|
| 0.01 | −0.0001 | 0.0025 | 0.0021 | 0.0014 | 0.0009 | 0.0003 |
| 0.03 | −0.0009 | 0.0097 | 0.0092 | 0.0083 | 0.010 | 0.0027 |
| 0.05 | −0.0025 | 0.0174 | 0.0181 | 0.0197 | 0.013 | 0.0075 |
| 0.10 | −0.0100 | 0.0368 | 0.042 | 0.048 | 0.046 | 0.0297 |
| 0.20 | −0.0406 | 0.059 | 0.092 | 0.116 | 0.128 | 0.1151 |
| 0.30 | −0.0929 | 0.059 | 0.111 | 0.169 | 0.209 | 0.2449 |
| 0.40 | −0.1695 | 0.018 | 0.098 | 0.195 | 0.266 | 0.3987 |
| 0.50 | −0.275 | −0.061 | 0.033 | 0.169 | 0.275 | 0.544 |
| 0.60 | −0.416 | −0.190 | −0.080 | 0.064 | 0.202 | 0.631 |
| 0.65 | −0.504 | −0.285 | −0.175 | −0.020 | 0.139 | 0.629 |
| 0.70 | −0.607 | −0.410 | −0.305 | −0.150 | 0.035 | 0.578 |
| 0.75 | −0.730 | −0.550 | −0.390 | −0.240 | −0.150 | 0.456 |
| 0.80 | −0.879 | −0.72 | −0.65 | −0.52 | −0.37 | 0.233 |
| 0.85 | −1.068 | −0.94 | −0.89 | −0.78 | −0.68 | −0.147 |
| 0.90 | −1.325 | −1.35 | −1.25 | −1.25 | −1.23 | −0.790 |
| 0.95 | −1.740 | −1.74 | −1.74 | −1.74 | −1.74 | −2.004 |
| 0.98 | −2.252 | −2.477 | −2.692 | −2.889 | −3.062 | −3.606 |
| 1.02 | −2.344 | −2.722 | −2.888 | −3.144 | −3.380 | −4.225 |
| 1.05 | −1.93 | −2.195 | −2.308 | −2.469 | −2.619 | −3.141 |
| 1.10 | −1.65 | −1.840 | −1.91 | −2.021 | −2.08 | −2.45 |
| 1.15 | −1.51 | −1.657 | −1.71 | −1.794 | −1.83 | −2.05 |
| 1.20 | −1.44 | −1.541 | −1.58 | −1.650 | −1.70 | −1.87 |
| 1.25 | −1.36 | −1.458 | −1.49 | −1.549 | −1.60 | −1.74 |
| 1.30 | −1.32 | −1.397 | −1.43 | −1.474 | −1.51 | −1.63 |
| 1.40 | −1.25 | −1.310 | −1.33 | −1.369 | −1.40 | −1.49 |
| 1.50 | −1.20 | −1.252 | −1.270 | −1.299 | −1.320 | −1.390 |
| 1.70 | −1.15 | −1.179 | −1.195 | −1.211 | −1.225 | −1.270 |
| 2.00 | −1.10 | −1.119 | −1.13 | −1.140 | −1.148 | −1.180 |
| 2.50 | −1.06 | −1.072 | −1.078 | −1.084 | −1.091 | −1.107 |
| 3.00 | −1.04 | −1.048 | −1.051 | −1.057 | −1.063 | −1.070 |
| 5.00 | −1.014 | −1.017 | −1.019 | −1.019 | −1.02 | −1.023 |
| 10.00 | −1.003 | −1.001 | −1.002 | −1.005 | −1.005 | −1.006 |
| 15.00 | −1.00 | −1.000 | −1.00 | −1.002 | −1.00 | −1.00 |

value gives for the full width at half maximum of the $q$-state $W_0=(2\pi c/\omega_q^2)\eta_0=0.118$ x.u. for all states of all atoms; whereas observed $K$-state widths, for example, vary from 0.70 x.u. (0.58 ev) for argon,[11] 0.15 x.u. (8 ev) for silver,[12] to 0.118 x.u. (62 ev) for gold;[13] and observed $L_{\rm I}$ widths are 4.6 x.u. (5.3 ev) for silver,[12] and 0.52 x.u. (8.7 ev) for gold.[13,14]

In general, $W_0$ is less than the observed widths, and two reasons are presented to account for the difference: First, the classical oscillation may be prematurely interrupted by the filling of the $q$-electron vacancy by another electronic transition (either radiative or non-radiative), and, second, the energy position of the $q$ state is broadened by splitting of the state into unresolved multiplet states due to interactions between the $q$ vacancy and outer electrons of the atom or neighboring atoms. The early interruption of the oscillation may properly be considered as contributing to $\eta_q$, but not the splitting of the state. The splitting is probably negligible for $K$ states for atoms $Z \gtrsim 16$ and for $L$ states for $Z \gtrsim 45$, except for the transition elements;[15] and, of

[11] L. G. Parratt, Phys. Rev. 56, 295 (1939).

[12] L. G. Parratt, Phys. Rev. 54, 99 (1938).

[13] F. K. Richtmyer, Revs. Modern Phys. 9, 391 (1937). The $K$ width for gold has not been directly measured; the value 62 ev is believed to be better than the value reported by Richtmyer.

[14] Previous discussions of the comparison of classical and observed widths have been in terms of emission lines; this is incorrect. It is evident from the integrated form of Eq. (3), that $\zeta(=\eta_q/\omega)$ refers to the width of the absorption edge or state.

[15] Widths of lines for transition elements have been measured for $K$ lines; e.g., see Fig. 6 of L. G. Parratt, Phys. Rev. 50, 1 (1936).

course, if the $q$ electrons are near the outer part of the atom in a solid the splitting may be very large.

The state width $W_q$ has not been measured for many $q$'s for many elements, but we may infer their values from measurements of emission line widths, making appropriate correction for the width of the final state, or by extrapolation from a nearby $Z$ whose $W_q$ has been measured (the energy width may be taken as proportional to $Z^4$ if it is not much greater than $W_0$). Thus, for example, $W_K$ for copper is about 0.30 x.u.; $W_{LI}$, $W_{LII}$ and $W_{LIII}$ for wolfram, 0.56, 0.27 and 0.40 x.u., respectively. $W_M$ and $W_N$ values are much larger because of non-radiative transitions.

To arrive at the value of $\eta_q$ for use in the above dispersion equations, we note that $\eta_0 \propto \omega^2$, and may become very large for $\omega \gg \omega_q$. For large $\omega/\omega_q$, the "premature" death of the $q$ state (filling by another process) is of no concern. For any $\omega/\omega_q$ and for any ratio $\eta_q/\eta_0$, we may write approximately

$$\eta_q = \eta_0\left\{1+\left(\frac{\omega_q}{\omega}\right)^2\left[\frac{W_q}{0.118}-1\right]\right\}, \qquad (21)$$
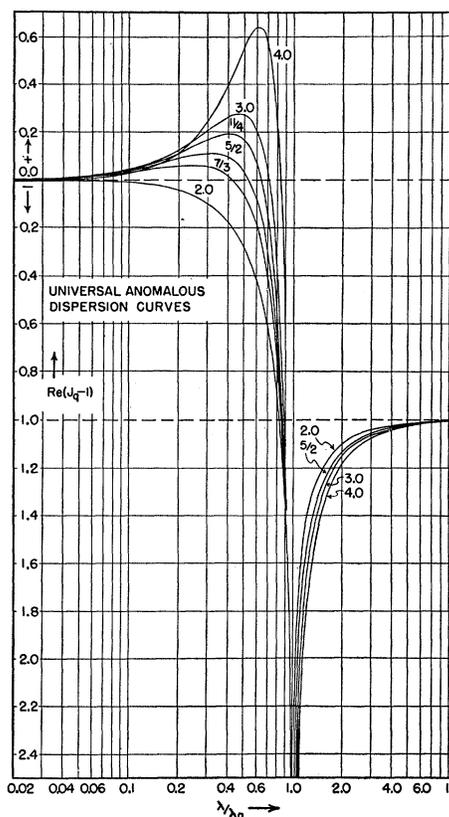
where $W_q$ is in x.u.



FIG. 1. The anomalous dispersion for any $q$ shell of electrons for any atom is equal to Re($J_q-1$) multiplied by the oscillator strength. Re($J_q-1$) may be taken from this curve for the appropriate $p_q$ value where $p_q$ is the parameter in the distribution of dispersion oscillators $C_q\lambda^{p_q}$. Curves for five different $p_q$ values are shown.

TABLE II. Dispersion calculations for copper $K$ region.

| Line | $\lambda$(A) | $\lambda/\lambda_K$ | $g_K$ Re($J_K$−1) | $g_{LI}$ Re($J_{LI}$−1) | $g_{LII,III}$ Re($J_{II,III}$−1) | $g_M$ Re($J_M$−1) | $\mu_l/\rho$ | $f_2$ | $f-f_0$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo $K\alpha_1$ | 0.709 | 0.514 | +0.209 | −0.005 | 0.083 | 0.013 | 52 | 1.37 | 0.332 |
| Pb $L\alpha_1$ | 1.175 | 0.852 | −1.097 | −0.014 | 0.156 | 0.026 | 198 | 3.16 | −0.752 |
| Ge $K\alpha_1$ | 1.254 | 0.910 | −1.793 | −0.016 | 0.168 | 0.029 | 234 | 3.49 | −1.390 |
| Zn $K\beta_1$ | 1.295 | 0.939 | −2.358 | −0.017 | 0.175 | 0.030 | 261 | 3.77 | −1.906 |
| Ir $L\alpha_1$ | 1.351 | 0.980 | −3.850 | −0.019 | 0.184 | 0.032 | 290 | 4.02 | −3.337 |
| Cu $K\beta_1$ | 1.392 | 1.010 | −4.949 | −0.020 | 0.190 | 0.034 | 38 | 0.51 | −4.740 |
| Zn $K\alpha_1$ | 1.435 | 1.041 | −3.471 | −0.022 | 0.196 | 0.035 | 42 | 0.55 | −3.255 |
| Cu $K\alpha_1$ | 1.541 | 1.117 | −2.565 | −0.025 | 0.213 | 0.039 | 51 | 0.62 | −2.349 |
| Ni $K\alpha_1$ | 1.658 | 1.202 | −2.187 | −0.029 | 0.231 | 0.043 | 62.8 | 0.71 | −1.932 |
| Co $K\alpha_1$ | 1.789 | 1.297 | −1.965 | −0.033 | 0.251 | 0.048 | 76 | 0.80 | −1.688 |
| Fe $K\alpha_1$ | 1.936 | 1.404 | −1.816 | −0.039 | 0.272 | 0.054 | 96.3 | 0.93 | −1.513 |
| Cr $K\alpha_1$ | 2.290 | 1.661 | −1.629 | −0.055 | 0.321 | 0.068 | 150 | 1.23 | −1.267 |

$$\lambda_K=1.379\text{A} \qquad p_K=11/4 \qquad g_K= 1.33 \qquad W_K=0.30 \text{ x.u.} \qquad \rho= 8.936$$
$$\lambda_{LI}= 12 \qquad p_{LI}=2 \qquad g_{LI}= 1.5 \qquad W_{LI}= 30 \qquad M=63.57$$
$$\lambda_{LII,III}= 13.15 \qquad p_{LII,III}=5/2 \qquad g_{LII,III}= 4 \qquad W_{LII,III}= 6$$
$$\lambda_M=160 \qquad p_M=5/2 \qquad g_M=20 \qquad W_M=2000$$

The only reliable method of knowing the relative effect of damping is to have the complete expressions and to make the necessary calculations. In the special cases of $p$ values shown below, an effort has been made to separate the damping terms so that, with $\eta_q$ known, their relative effects can be readily seen.

### SPECIAL CASES OF $p$ VALUES

For $p$ (or $\alpha$) equal to an integer, the integration for $J_q$ is readily carried out as already discussed. In this section we shall give examples for $p=7/3$, $5/2$, and $11/4$.

In the following formulas, 2nd and higher powers of $\zeta$ have been neglected compared to unity except where important, and the terms have been written in a form intended to make calculations easy.

### $p=7/3$

For this case, $n=2$ and $m=3$. For $|z| \leqslant 1$,

$$\text{Re}[J_q-1]_{7/3}{}^{\text{I}}= -\frac{2a^2}{3}\left[\frac{1}{2}\ln\left(\frac{1+a+a^2}{1-2a\cos\frac{1}{3}\theta+a^2}\right)\right.$$

$$+\sqrt{3}\,\tan^{-1}\left(\frac{\sqrt{3}a}{2+a}\right)-\frac{\pi}{\sqrt{3}}\left(1-\frac{5\zeta}{\sqrt{3}}\right)$$

$$\left.-\frac{5\zeta}{3}\tan^{-1}\left(\frac{a\sin\frac{1}{3}\theta}{1-a\cos\frac{1}{3}\theta}\right)\right]. \quad (22)$$

For $|z| \geqslant 1$,

$$\text{Re}[J_q-1]_{7/3}{}^{\text{II}}= -\frac{2}{3b^2}\left[\frac{1}{2}\ln\left(\frac{1+b+b^2}{1-2b\cos\frac{1}{3}\theta+b^2}\right)\right.$$

$$\left.-\sqrt{3}\,\tan^{-1}\left(\frac{\sqrt{3}b}{2+b}\right)+\frac{5\zeta}{3}\tan^{-1}\left(\frac{b\sin\frac{1}{3}\theta}{1-b\cos\frac{1}{3}\theta}\right)\right]. \quad (23)$$

### $p=5/2$

For this case, $n=3$ and $m=4$. For $|z| \leqslant 1$

$$\text{Re}[J_q-1]_{5/2}{}^{\text{I}}= -\frac{3a^3}{4}\left\{\frac{1}{2}\ln\left[\frac{(1+a)^2}{1-2a\cos\frac{1}{4}\theta+a^2}\right]\right.$$

$$\left.+2\tan^{-1}a-\pi\left(1-\frac{7\zeta}{4}\right)-\frac{7\zeta}{4}\tan^{-1}\left(\frac{a\sin\frac{1}{4}\theta}{1-a\cos\frac{1}{4}\theta}\right)\right\}. \quad (24)$$

For $|z| \geqslant 1$,

$$\text{Re}[J_q-1]_{5/2}{}^{\text{II}}= -\frac{3}{4b^3}\left\{\frac{1}{2}\ln\left[\frac{(1+b)^2}{1-2b\cos\frac{1}{4}\theta+b^2}\right]\right.$$

$$\left.-2\tan^{-1}b+\frac{7\zeta}{4}\tan^{-1}\left(\frac{b\sin\frac{1}{4}\theta}{1-b\cos\frac{1}{4}\theta}\right)\right\}. \quad (25)$$

Note that in this case $p=5/2$, if damping is assumed to be zero, Eq. (1) or (7) can be integrated directly, since $p$ is a half-integer.[3] The value for $\delta_q$ obtained from Eqs. (25) and (16), when $\zeta=0$, is identical with the value reported by Williams.[3]

### $p=11/4$

For this case, $n=7$ and $m=8$. For $|z| \leqslant 1$

$$\text{Re}[J_q-1]_{11/4}{}^{\text{I}}= -\frac{7a^7}{8}\left\{\frac{1}{2}\ln\left[\frac{(1+a)^2}{1-2a\cos\frac{1}{8}\theta+a^2}\right]\right.$$

$$+\frac{1}{\sqrt{2}}\ln\left(\frac{1+\sqrt{2}a+a^2}{1-\sqrt{2}a+a^2}\right)+2\tan^{-1}a$$

$$+\sqrt{2}\,\tan^{-1}\left(\frac{\sqrt{2}a}{1-a^2}\right)-\pi\cot\frac{1}{8}\pi\left(1-\frac{15\zeta}{8}\tan\frac{1}{8}\pi\right)$$

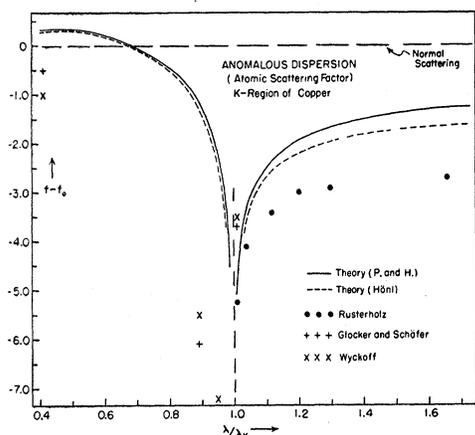$$\left.-\frac{15\zeta}{8}\tan^{-1}\left(\frac{a\sin\frac{1}{8}\theta}{1-a\cos\frac{1}{8}\theta}\right)\right\}. \quad (26)$$

FIG. 2. Comparison of calculated and measured scattering factors (at zero angle) for copper in the $K$ region.

For $|z| \gg 1$,

$$\mathrm{Re}[J_q - 1]_{11/4}{}^{\mathrm{II}} = -\frac{7}{8b^7}\left\{\frac{1}{2}\ln\left[\frac{(1+b)^2}{1-2b\cos\frac{1}{8}\theta+b^2}\right]\right.$$

$$+\frac{1}{\sqrt{2}}\ln\left(\frac{1+\sqrt{2}b+b^2}{1-\sqrt{2}b+b^2}\right)-2\tan^{-1}b$$

$$\left.-\sqrt{2}\tan^{-1}\left(\frac{\sqrt{2}b}{1-b^2}\right)+\frac{15\zeta}{8}\tan^{-1}\left(\frac{b\sin\frac{1}{8}\theta}{1-b\cos\frac{1}{8}\theta}\right)\right\}. \quad (27)$$

In each of these cases the closed form of the sum has been used, but the open form may be the more convenient except when $x$ is between about $\frac{1}{2}$ and 2 depending upon the desired accuracy.

## UNIVERSAL ANOMALOUS DISPERSION CURVES

By evaluation of the above equations, we see that the term $\zeta$ is of the order of $2\times10^{-3}$ or less, sufficiently
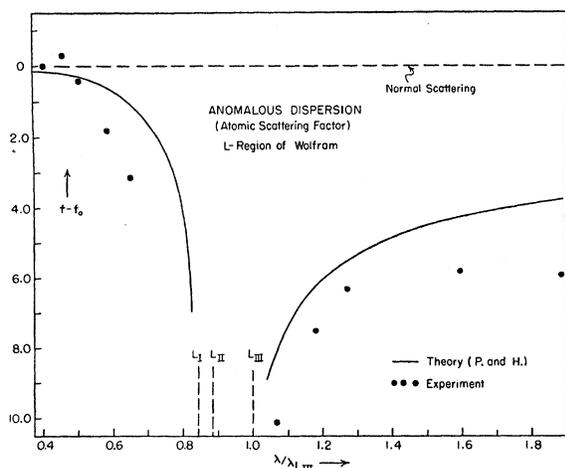


FIG. 3. Comparison of calculated and measured scattering factors (at zero angle) for wolfram in the $L$ region.

small that it can be neglected in all cases where $\lambda/\lambda_q$ differs from unity by more than $10^{-4}$ (or $10^{-5}$ in most cases). In general, no oscillator strength $g_q$ is meaningfully known as well as one part in $10^3$, nor is the ratio $\lambda/\lambda_q$ meaningfully known as well as about one part in $10^4$ (because of the large intrinsic line width, and because of unresolved structure in the absorption edge). Thus, for practically all experimental problems in anomalous dispersion, we may write

$$a = \frac{1}{b} = \left(\frac{\lambda}{\lambda_q}\right)^{2/m}\left(1+\frac{\zeta^2}{2m}+\cdots\right) \doteq \left(\frac{\lambda}{\lambda_q}\right)^{2/m} \quad (28)$$

and

$$\cos(\theta/m) \doteq 1 - (\zeta^2/2m^2) \doteq 1, \quad (29)$$

and introduce thereby a negligible error, less than about 0.2 percent.

With damping neglected, $\mathrm{Re}(J_q-1)$ is independent of the atomic number and of the particular electron shell, and depends upon only $p_q$. Curves of $\mathrm{Re}(J_q-1)$ vs $\lambda/\lambda_q$ for various values of $p_q$ are therefore universal anomalous dispersion curves; and if $p_q$ and $g_q$ are known, the magnitude of the anomalous dispersion for each $q$-shell of electrons in any atom can be readily deduced therefrom. The calculations for such curves are presented in Table I for five different $p_q$ values, and the curves are shown in Fig. 1. Interpolation for an intermediate $p_q$ value is possible.

If we wish numerical values of anomalous dispersion when $\lambda/\lambda_q$ is within $10^{-4}$ or $10^{-5}$ of unity, we must revert to the equations and retain the damping factor.

## CALCULATIONS

For comparison with theoretical values, we shall use experimental measurements of $f-f_0$ for iron,[16] copper[17] and for wolfram.[18] The wavelengths used in these experiments are not sufficiently close to $\lambda_q$ to warrant inclusion of the damping factor.

Table II lists calculations for copper. The $f-f_0$ values are compared with experiment in Fig. 2. The constants used in the calculations are given under the table. The calculated curve from Hönl's theory for $K$ electrons is also shown in the figure.

(For comparison with the two $L$ subgroups listed in Table II, we have also calculated $g_L \, \mathrm{Re}(J_L-1)$ for the $L$ electrons as a single group with $p_L=7/3$. The difference ranges from 21 percent at 0.709A to 10 percent at 2.290A.)

For the wavelengths of Table II, the largest $\zeta$ value is $\zeta_K = 5.4\times10^{-4}$ at 0.709A, and smallest the is $\zeta_K = 0.40 \times10^{-4}$ at 2.290A.

[16] R. Glocker and K. Schäfer, Z. Physik **73**, 289 (1931) and **86**, 738 (1933); and R. W. G. Wyckoff, Phys. Rev. **36**, 1116 (1930). The corrected observed values of $f$ are subtracted from the Thomas-Fermi $f_0=17.3$ for the (110) planes of Fe.
[17] A. A. Rusterholz, Z. Physik **82**, 538 (1933).
[18] J. Brentano and A. Baxter, Z. Physik **89**, 720 (1934).

TABLE III. Dispersion calculations for wolfram $L$ region.

| Line | $\lambda$(A) | $\lambda/\lambda_{LIII}$ | $g_K$ Re($J_K-1$) | $g_{LI}$ Re($J_{LI}-1$) | $g_{LII}$ Re($J_{LII}-1$) | $g_{LIII}$ Re($J_{LIII}-1$) | $g_M$ Re($J_M-1$) | $g_N$ Re($J_N-1$) | $\mu_l/\rho$ | $f_2$ | $f-f_0$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sn $K\alpha_1$ | 0.491 | 0.404 | −1.284 | −0.052 | 0.086 | 0.234 | 0.679 | 0.061 | 36 | 3.98 | 0.150 |
| Ag $K\alpha_1$ | 0.560 | 0.461 | −1.266 | −0.156 | 0.020 | 0.165 | 0.813 | 0.074 | 52 | 5.04 | −0.178 |
| Rh $K\alpha_1$ | 0.613 | 0.505 | −1.259 | −0.266 | −0.049 | 0.082 | 0.902 | 0.084 | 68 | 6.01 | −0.260 |
| Mo $K\alpha_1$ | 0.709 | 0.584 | −1.247 | −0.536 | −0.239 | −0.143 | 1.059 | 0.104 | 104 | 7.94 | −0.572 |
| Zr $K\alpha_1$ | 0.786 | 0.647 | −1.236 | −0.851 | −0.466 | −0.411 | 1.179 | 0.120 | 137 | 9.44 | −1.052 |
| Th $L\alpha_1$ | 0.956 | 0.788 | −1.222 | −2.305 | −1.444 | −1.422 | 1.425 | 0.158 | 238 | 13.49 | −3.508 |
| Zn $K\beta_1$ | 1.295 | 1.067 | −1.214 | −2.014 | −1.889 | −5.128 | 1.808 | 0.241 | 107 | 4.48 | −8.045 |
| Zn $K\alpha_1$ | 1.435 | 1.182 | −1.211 | −1.833 | −1.668 | −3.904 | 1.912 | 0.277 | 141 | 5.32 | −6.218 |
| Cu $K\alpha_1$ | 1.541 | 1.269 | −1.209 | −1.750 | −1.573 | −3.522 | 1.967 | 0.305 | 172 | 6.05 | −5.513 |
| Fe$K\alpha_1$ | 1.936 | 1.595 | −1.206 | −1.591 | −1.399 | −2.948 | 1.967 | 0.415 | 303 | 8.48 | −4.245 |
| Cr$K\alpha_1$ | 2.290 | 1.886 | −1.204 | −1.529 | −1.332 | −2.755 | 1.649 | 0.521 | 470 | 11.12 | −3.764 |

$$\lambda_K = 0.179\text{A} \quad p_K = 11/4 \quad g_K = 1.2 \quad\quad\quad \rho = 19.30$$
$$\lambda_{LI} = 1.024 \quad p_{LI} = 7/3 \quad g_{LI} = 1.4 \quad W_{LI} = 0.56\text{ x.u.} \quad M = 183.92$$
$$\lambda_{LII} = 1.074 \quad p_{LII} = 5/2 \quad g_{LII} = 1.2 \quad W_{LII} = 0.27$$
$$\lambda_{LIII} = 1.214 \quad p_{LIII} = 5/2 \quad g_{LIII} = 2.4 \quad W_{LIII} = 0.40$$
$$\lambda_M = 5.51 \quad p_M = 5/2 \quad g_M = 18 \quad W_M = 20$$
$$\lambda_N = 56 \quad p_N = 5/2 \quad g_N = 36 \quad W_N = 1200$$

Table III lists calculations for wolfram, and comparison with experiment is shown in Fig. 3. Again the constants used are given under the table. The $L$ electrons are subdivided; the $M$ and $N$ electrons are not. The oscillator strengths used here, as in the copper calculations, are selected on an arbitrary weighted average basis from theory and experiment,[5,8,19] as are also the $p_q$ values. Since $f_2$ is of minor importance, the electron shells are not subdivided for $\beta$.

For the wavelengths of Table III, the largest $\zeta$ value is $\zeta_M = 15.5 \times 10^{-4}$ at 2.290A, the smallest is $\zeta_{LII} = 2.5 \times 10^{-4}$ at 0.786A.

For such cases as this one for wolfram, the magnitude of Re($J_K$) is sometimes assumed to be zero and the normal dispersion reckoned as $\delta = A\lambda^2(Z-g_K)$ of $f_0 = Z-g_K$. Were this done, the $f-f_0$ scale of Fig. 3 would be dropped by 1.2 units and the calculated curve would go above $f-f_0 = 0$, as it does for the copper case.

Wavelengths for both tables are taken from Cauchois and Hulubei.[20]

So-called normal dispersion refers to a region of wavelengths for which $f-f_0$ is a constant; whether this constant is zero or $g_K$ (or $g_K+g_L$, etc.) is not now important. It is seen from the above calculations that the anomalous contributions from various electron shells, in addition to the particular shell whose $\lambda_q$ is in the wavelength region under study, is rarely negligible—

[19] The $M$-oscillator strength is, on one hand, less than the number of $M$-type electrons because of virtual transitions from outer shells, but, on the other hand, it is augmented by virtual transitions to inner shells. It is estimated that the increase is greater than the reduction for copper, and about equal for wolfram.

[20] Y. Cauchois and H. Hulubei, Longueurs d'Onde des Emissions X et des Discontinuités d'Absorption X (Hermann and Company, Paris, 1947). For copper, $\lambda_K$ is taken as 1.379A, about 9 ev less energy than is reported in this reference, for the reason mentioned in footnote 7 [also see Fig. 6 of W. W. Beeman and H. Friedman, Phys. Rev. 56, 392 (1939)].

there is practically no region of normal dispersion. This is illustrated in Fig. 4 for the entire region $0.1 < \lambda < 100$A for copper.

## SUMMARY

The distribution of "dispersion" oscillators in an atom can be written generally as the sum of $n$ terms of the form $C_{qn}\lambda^{p_{qn}}$. This distribution appears in a complex integrand in the expression for x-ray dispersion (either for the refractive index or for the scattering factor). The general integration of any term of this distribution has been carried out.

Damping of the oscillators has been retained in the integration, and the resulting equations allow ready evaluation of the numerical effect of damping. For practically all of the dispersion region, the damping can be neglected with an error of less than 0.2 percent. Then, universal anomalous dispersion curves can be used to determine Re($J_q-1$) which, when multiplied by the
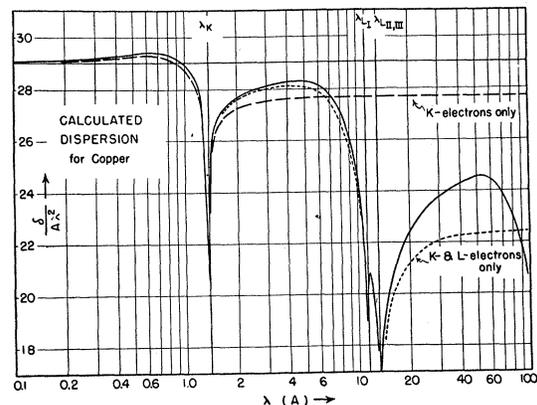


FIG. 4. There is practically no region of normal dispersion when several electron shells are included in the calculations.

oscillator strength and summed over all $q$ shells, gives easily and quickly the anomalous dispersion for any atom.

Sample calculations for the $K$ region of copper and for the $L$ region of tungsten have been made, using in each case only one term in the oscillator distribution for

each $q$ shell. Comparison with experiment shows less satisfactory agreement than with the previous less exact calculations. This disagreement is believed to be due to (a) the difficulties inherent in the experimental measurements, and (b) neglect of parts of the calculations in previous comparisons.

# Studies of Atomic Self-Consistent Fields. II. Interpolation Problems*

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(Received November 27, 1953)

By studying the self-consistent-field (SCF) functions tabulated in the literature, it is shown that a quantity, which for a hydrogenlike function would equal the atomic number $Z$, for SCF functions will represent a form of "effective nuclear charge" $Z_{eff}$, which for a series of consecutive atoms or ions appears to be an almost linear function of the atomic number, convenient for interpolation purposes. The positions and magnitudes of maxima and minima, nodes, derivatives in origin, eigenvalues, etc., are investigated by considering the corresponding effective nuclear charges. It is important that the nodes may be interpolated separately, since the logarithm of an SCF function, divided by a polynomial having the same zero points as the function itself, may be used for interpolating SCF functions as a whole. This logarithm may also be used for defining a continuously varying effective charge $Z_{eff}(r)$, which is convenient for interpolation purposes or for estimating fields with exchange from those without exchange.

THE numerical work involved in each cycle of the integration of the Hartree-Fock equations for atomic self-consistent fields (SCF) with exchange by using the technique developed by Hartree[1] is quite large, and, in order to secure a rapid convergence of the process, it is therefore important to have as good "initial" functions as possible. For this purpose it is now possible to utilize the properties of already tabulated fields; Hartree has shown that rather good estimates of the initial functions could be obtained simply by interpolating their departures from properly scaled hydrogenlike wave functions. A function $F(r)$ is here said to be obtained from another $f(r)$ by change of a scale factor $\lambda$, if

$$F(r) = \lambda^{\frac{3}{2}} f(\lambda r), \qquad (1)$$

which transformation leaves the normalization integral invariant.

Brown, Bartlett, and Dunn[2,3] have shown that the SCF wave functions can be approximately transformed into each other by using scale factors $\lambda$, which are obtained from the reciprocals of the positions of the maxima and minima of the tabulated functions and which appear to be almost linear functions of the atomic

number $Z$. Hartree and Hartree[4] have used a similar idea for scaling the departure of the SCF functions with exchange from those without exchange. In a slightly modified form, the scaling method has recently been used also by Scherr[5] in Chicago.

Using a somewhat different approach, Arnot and McLauchlan[6] and Manning and Millman[7] have shown that, instead of the wave functions themselves, the effective nuclear charges associated with the SCF potentials may be used for interpolation purposes. On a large-scale basis, these total charges have recently been tabulated by Freeman[8] for all fields available.

In the first paper of this series,[9] it was shown that SCF wave functions could be interpolated (and to some extent extrapolated) with a surprisingly high accuracy by means of analytic expressions of Slater type. The purpose of the present paper is to investigate whether it is possible to carry out similar interpolations directly in the numerical tables of the functions involved, without the help of the analytic forms. We will first show the existence of some simple regularities for quantities like the positions and the magnitudes of maxima and minima, derivatives in origin, nodes,

[1] For a survey, see D. R. Hartree, Repts. Progr. in Phys. **11**, 113 (1946).
[2] Brown, Bartlett, and Dunn, Phys. Rev. **44**, 296 (1933).
[3] See also Hartree, reference 1, p. 126, Fig. 1, for another example.
[4] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).
[5] C. W. Scherr, J. Chem. Phys. **21**, 1237, 1241 (1953).
[6] F. L. Arnot and J. C. McLauchlan, Proc. Roy. Soc. (London) **A146**, 662 (1934).
[7] M. F. Manning and J. Millman, Phys. Rev. **49**, 848 (1936).
[8] A. J. Freeman, Phys. Rev. **91**, 1410 (1953).
[9] P. O. Löwdin, Phys. Rev. **90**, 120 (1953), in the following referred to as Part I.