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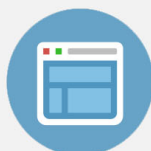
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# Relativistic Calculation of Anomalous Scattering Factors for X Rays\*

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Anomalous scattering factors  $\Delta f'$  and  $\Delta f''$  have been calculated relativistically for Cr, Fe, Cu, Mo, and Ag  $K_\alpha$  radiations for the atoms Li through Cf. An interpolation scheme for other wavelengths is included in a separate report. Relativistic calculations of the photoelectric cross section have been made and the integral for the principal contribution to  $\Delta f'$  has been evaluated numerically without approximation to the form of the cross section-vs-energy curve, as has been done in previous calculations. Many of the results are significantly different from previous calculations. Where experimental values exist, agreement for  $\Delta f''$  is improved. For the rare gases, except for xenon, agreement between  $\Delta f'$  and experiment is improved. Because of the more rigorous evaluation of  $\Delta f'$  from cross-section information, it is presumed that the present  $\Delta f'$  values are more accurate than previous calculated values. Calculated mass absorption coefficients for the elements are included as incidental information.

## I. INTRODUCTION

In 1965 an extensive calculation of anomalous x-ray scattering factors  $\Delta f'$  and  $\Delta f''$  was published by Cromer.<sup>1</sup> The method used in making those calculations was the same as that given by James,<sup>2</sup> developed in a more general form by Parratt and Hempstead,<sup>3</sup> and later used by Dauben and Templeton<sup>4</sup> and by Templeton.<sup>5</sup> The major improvement by Cromer<sup>1</sup> was in the use of relativistic wavefunctions to compute the oscillator strengths required by the method.

In all these previous calculations an approximation was made concerning the variation of the photoelectric absorption coefficient, or cross section, with energy. This approximation,

$$\sigma(\omega) = (\omega_k/\omega)^n \sigma(\omega_k), \quad (1)$$

where  $\sigma(\omega)$  is the cross section at energy  $\omega$  and  $\omega_k$  is the binding energy of the electron, was used for two reasons: (1) The variation of the cross section with energy, although not well known, was believed to be approximately of this form, and (2) this functional form made it possible to integrate the function for  $\Delta f'$  in closed form. The value of  $n$  in Eq. (1) was assumed to be 11/4 for the 1s 1/2 orbital, 7/3 for the 2s 1/2 orbital, and 5/2 for all other orbitals. The constant,  $\sigma(\omega_k)$ , can be obtained from the oscillator strength.<sup>2</sup> The use of Eq. (1) was recognized<sup>1</sup> as a basic flaw in the method, and the present calculations were undertaken to remove this approximation.

## II. THEORY

The scattering amplitude for light by a bound electron is, according to relativistic quantum theory,<sup>6</sup>

$$S_{i \rightarrow f} = -2\pi i \delta(\epsilon_1 + \hbar\omega_1 - \epsilon_2 - \hbar\omega_2) \cdot [4\pi(e\hbar c)^2/2mc^2\hbar(\omega_1\omega_2)^{1/2}] f,$$

where

$$f = mc^2 \sum_{n^+} \left( \frac{\langle 2 | \mathbf{e}_2 \cdot \boldsymbol{\alpha} \exp(-i\mathbf{k}_2 \cdot \mathbf{r}) | n^+ \rangle \langle n^+ | \mathbf{e}_1 \cdot \boldsymbol{\alpha} \exp(i\mathbf{k}_1 \cdot \mathbf{r}) | 1 \rangle}{\epsilon_1 - \epsilon_{n^+} + \hbar\omega_1} + \frac{\langle 2 | \mathbf{e}_1 \cdot \boldsymbol{\alpha} \exp(i\mathbf{k}_1 \cdot \mathbf{r}) | n^+ \rangle \langle n^+ | \mathbf{e}_2 \cdot \boldsymbol{\alpha} \exp(-i\mathbf{k}_2 \cdot \mathbf{r}) | 1 \rangle}{\epsilon_1 - \epsilon_{n^+} - \hbar\omega_2} \right) \\ + mc^2 \sum_{n^-} \left( \frac{\langle 2 | \mathbf{e}_2 \cdot \boldsymbol{\alpha} \exp(-i\mathbf{k}_2 \cdot \mathbf{r}) | n^- \rangle \langle n^- | \mathbf{e}_1 \cdot \boldsymbol{\alpha} \exp(i\mathbf{k}_1 \cdot \mathbf{r}) | 1 \rangle}{\epsilon_2 + |\epsilon_{n^-}| + \hbar\omega_2} + \frac{\langle 2 | \mathbf{e}_1 \cdot \boldsymbol{\alpha} \exp(i\mathbf{k}_1 \cdot \mathbf{r}) | n^- \rangle \langle n^- | \mathbf{e}_2 \cdot \boldsymbol{\alpha} \exp(-i\mathbf{k}_2 \cdot \mathbf{r}) | 1 \rangle}{\epsilon_2 + |\epsilon_{n^-}| - \hbar\omega_1} \right). \quad (2)$$

$f$  is the desired scattering factor;  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are the polarization vectors, and  $\mathbf{k}_1$  and  $\mathbf{k}_2$  the wave vectors of the incident and scattered light;  $\omega_1$  and  $\omega_2$  are the corresponding angular frequencies;  $\boldsymbol{\alpha}$  is the Dirac velocity operator; 1 and 2 are the initial and final states of the electron; and  $n^+$  and  $n^-$  indicate intermediate electron states of positive and negative energy. The sums are over all positive and negative intermediate states except those positive energy states occupied by other atomic electrons. A further sum must be taken over all the electrons of the atom, but this will not be indicated explicitly in most of the following formulas.

To put  $f$  into a form which resembles the nonrelativistic scattering factor more closely and which is simpler for computational purposes, we write

$$f = f_0 + (f - f_0), \quad (3)$$

where  $f_0$  is defined by an equation like Eq. (2), except that all energy denominators are replaced by  $2mc^2$ , and

the sums over  $n^+$  and  $n^-$  include all states without exception. Since the set of intermediate states is complete,

$$f_0 = mc^2 \langle 2 | (\mathbf{e}_2 \cdot \boldsymbol{\alpha} \mathbf{e}_1 \cdot \boldsymbol{\alpha} + \mathbf{e}_1 \cdot \boldsymbol{\alpha} \mathbf{e}_2 \cdot \boldsymbol{\alpha}) \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}] | 1 \rangle / 2mc^2 \\ = \mathbf{e}_1 \cdot \mathbf{e}_2 \langle 2 | \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}] | 1 \rangle. \quad (4)$$

$f_0$  is the main part of the scattering factor for x rays. The remaining anomalous terms are treated as follows. Let the two sums in Eq. (2) be called  $f^+$  and  $f^-$  and let  $f_0$  be similarly decomposed. Then Eq. (3) may be rewritten as

$$f = f_0 + f^+ - f_0^+ + (f^- - f_0^-). \quad (5)$$

$f^+$  is the largest of the anomalous terms and will be evaluated by being related to the photoelectric cross section as indicated below;  $f_0^+$  is small and may be evaluated by making the nonrelativistic approximation and considering only the electric dipole contributions; and  $f^- - f_0^-$  is of similar size and is evaluated by using the same approximations.

For a particle obeying the Dirac equation,

$$(c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V - \epsilon)\psi = 0, \quad (6)$$

where

$$\psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix}, \quad (7)$$

the nonrelativistic approximation (to the order of accuracy needed here) consists, for positive energy states, in setting

$$\epsilon^+ = mc^2 + E^+, \\ H^+ \phi = E^+ \phi, \quad H^+ = p^2/2m + V, \\ \chi = c\boldsymbol{\sigma} \cdot \mathbf{p} \phi / 2mc^2; \quad (8)$$

and, for negative energy states,

$$\epsilon^- = -mc^2 - E^-, \\ H^- \chi = E^- \chi, \quad H^- = p^2/2m - V, \\ \phi = -c\boldsymbol{\sigma} \cdot \mathbf{p} \chi / 2mc^2. \quad (9)$$

The solutions of  $H^+ \phi = E^+ \phi$  and  $H^- \chi = E^- \chi$  form complete sets of eigenfunctions.

The electric dipole approximation assumes that  $1/|\mathbf{k}|$  is much larger than orbital dimensions and permits the replacement of  $\exp(i\mathbf{k} \cdot \mathbf{r})$  by 1.

In evaluating the anomalous terms  $f^+$ ,  $-f_0^+$ , and  $(f^- - f_0^-)$ , we limit ourselves to coherent, nearly forward scattering. Then

State 1 = State 2,

$$\omega_1 = \omega_2, \\ |\mathbf{k}_1| = |\mathbf{k}_2| \gg |\mathbf{k}_1 - \mathbf{k}_2|, \\ \mathbf{e}_1 \approx \mathbf{e}_2. \quad (10)$$

The subscripts 1 and 2 will be dropped from  $\omega$ ,  $\mathbf{k}$ , and  $\mathbf{e}$ .

Turning now to  $f_0^+$  we have

$$f_0^+ = mc^2 \sum_{n^+} |\langle n^+ | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2 / 2mc^2. \quad (11)$$

In each matrix element there are two terms of equal magnitude: one involving the large component of  $|n^+\rangle$  and the small component of  $|1\rangle$ , and the other involving the small component of  $|n^+\rangle$  and the large component of  $|1\rangle$ . Using the electric dipole approximation and Eq. (8), we get

$$f_0^+ = \sum_n |\langle \phi_n | (\boldsymbol{\sigma} \cdot \mathbf{e} \boldsymbol{\sigma} \cdot \mathbf{p} + \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{e}) / 2mc | \phi_1 \rangle|^2 \\ = \langle \phi_1 | (\boldsymbol{\sigma} \cdot \mathbf{e} \boldsymbol{\sigma} \cdot \mathbf{p} + \boldsymbol{\sigma} \cdot \mathbf{p} \boldsymbol{\sigma} \cdot \mathbf{e})^2 / 4m^2 c^2 | \phi_1 \rangle \\ = \langle \phi_1 | (\mathbf{e} \cdot \mathbf{p} / mc)^2 | \phi_1 \rangle. \quad (12)$$

If an average over polarization is now taken,  $f_0^+$  is reduced to

$$f_0^+ = 2/3 mc^2 \langle \phi_1 | p^2 / 2m | \phi_1 \rangle. \quad (13)$$

Thus  $f_0^+$  is expressed in terms of the electron kinetic energy. If a sum over all electrons is now taken, we get

$$(-f_0^+)_{\text{tot}} = -2T_{\text{tot}}/3mc^2. \quad (14)$$

The total kinetic energy,  $T_{\text{tot}}$ , is related by the virial theorem for Coulomb forces to the total energy of the atom by

$$T_{\text{tot}} = -E_{\text{tot}}, \quad (15)$$

and the latter is available from self-consistent field calculations.

Next consider the other small anomalous term

$$f^- - f_0^- = mc^2 \sum_n |\langle n^- | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2 [(\epsilon_1 + |\epsilon_n^-| + \hbar\omega)^{-1} - (2mc^2)^{-1} + (\epsilon_1 + |\epsilon_n^-| - \hbar\omega)^{-1} - (2mc^2)^{-1}]. \quad (16)$$

The bracketed energy denominators are, in the nonrelativistic approximation,

$$-2[(E_1 - E_n^-)/(2mc^2)^2]. \quad (17)$$

In the matrix elements the only important terms involve  $\phi_1$  for the atomic electron states and  $\chi_n$  for the negative energy states. Again using the electric dipole term only, we get

$$\begin{aligned} f^- - f_0^- &= mc^2 \sum_n |\langle \chi_n | \boldsymbol{\sigma} \cdot \mathbf{e} | \phi_1 \rangle|^2 \{-2[(E_1 + E_n^-)/(2mc^2)^2]\} \\ &= - \sum_n \langle \phi_1 | \boldsymbol{\sigma} \cdot \mathbf{e} | \chi_n \rangle \langle \chi_n | (H^+ + H^-) \boldsymbol{\sigma} \cdot \mathbf{e} | \phi_1 \rangle / 2mc^2 \\ &= - \langle \phi_1 | (\boldsymbol{\sigma} \cdot \mathbf{e})^2 (H^+ + H^-) | \phi_1 \rangle / 2mc^2 \\ &= - \langle \phi_1 | p^2 / 2m | \phi_1 \rangle / mc^2. \end{aligned} \quad (18)$$

So  $(f^- - f_0^-)$  is the same as  $-f_0^+$  except for a constant factor, and the same is true for the total contribution to the scattering factor. The sum of the two small anomalous terms for all the electrons in an atom is

$$(-f_0^+ + f^- - f_0^-)_{\text{tot}} = 5E_{\text{tot}}/3mc^2. \quad (19)$$

The principal anomalous term, for the case of coherent, nearly forward scattering, is

$$f^+ = mc^2 \sum_{n^+} |\langle n^+ | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2 [(\epsilon_1 - \epsilon_n^+ + \hbar\omega)^{-1} + (\epsilon_1 - \epsilon_n^+ - \hbar\omega)^{-1}]. \quad (20)$$

There are contributions from both unoccupied bound states and continuum states, but the contribution from the unoccupied bound states is small and will be omitted. An estimate of these terms will be given later.

The sum over the continuum states, when they are properly normalized, is

$$f^+ = mc^2 \int_{mc^2}^{\infty} |\langle \epsilon^+ | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2 [(\epsilon_1 - \epsilon^+ + \hbar\omega)^{-1} + (\epsilon_1 - \epsilon^+ - \hbar\omega)^{-1}] d\epsilon^+. \quad (21)$$

The first energy denominator has a singularity if  $\hbar\omega$  exceeds the electron binding energy. The treatment for the singular integral is well known from scattering theory. The amplitude of the initial state decreases with time because of depletion due to the scattering. Thus the time dependence in the absence of scattering,  $\exp(-i\epsilon_1 t/\hbar)$ , is changed to  $\exp[-i(\epsilon_1 - i\gamma)t/\hbar]$ , where  $\gamma$  is a very small positive number. The singular factor in the integral is changed in the same way:

$$(\epsilon_1 - \epsilon^+ + \hbar\omega)^{-1} \rightarrow (\epsilon_1 - i\gamma - \epsilon^+ + \hbar\omega)^{-1} = P(\epsilon_1 - \epsilon^+ + \hbar\omega)^{-1} + i\pi\delta(\epsilon_1 - \epsilon^+ + \hbar\omega), \quad (22)$$

where  $P$  indicates that the principal value of the integral is to be taken and  $\delta$  is the Dirac delta function. The imaginary part arises from the part of the contour of integration which is close to and just above the singularity. It is the mathematical origin of the imaginary part of the dispersion,  $\Delta f''$ .

The frequency dependent scattering,  $f^+$ , neglecting transitions to the unoccupied bound states, is then given by

$$\begin{aligned} mc^2 \left( P \int_{mc^2}^{\infty} \frac{|\langle \epsilon^+ | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2}{\epsilon_1 - \epsilon^+ + \hbar\omega} d\epsilon^+ \right. \\ \left. + \int_{mc^2}^{\infty} \frac{|\langle \epsilon^+ | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2}{\epsilon_1 - \epsilon^+ - \hbar\omega} d\epsilon^+ + i\pi |\langle \epsilon_1 + \hbar\omega | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2 \right) \\ = mc^2 \left( P \int_{mc^2}^{\infty} \frac{2(\epsilon^+ - \epsilon_1) |\langle \epsilon^+ | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2}{(\hbar\omega)^2 - (\epsilon^+ - \epsilon_1)^2} + i\pi |\langle \epsilon^+ + \hbar\omega | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2 \right). \end{aligned} \quad (23)$$

The photoelectric cross section is<sup>6</sup>

$$\sigma(\hbar\omega) = (4\pi^2 e^2 m / c\omega) \cdot mc^2 |\langle \epsilon_1 + \hbar\omega | \mathbf{e} \cdot \boldsymbol{\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}) | 1 \rangle|^2. \quad (24)$$

The matrix element in Eq. (24) is the same as that in the imaginary part of Eq. (23), and  $\Delta f''$  is, therefore, given by

$$\Delta f'' = (mc/4\pi\hbar e^2) (\hbar\omega) \sigma(\hbar\omega). \quad (25)$$

Equation (25), although expressed in terms of the cross section rather than the oscillator strength, is the same as given by James.<sup>2</sup> The real part of  $f^+$  can also be expressed in terms of the cross section and is

$$f^+ = \left( \frac{mc}{2\pi^2\hbar e^2} \right) P \int_{mc^2}^{\infty} \frac{(\epsilon^+ - \epsilon_1)^2 \sigma(\epsilon^+ - \epsilon_1) d\epsilon^+}{(\hbar\omega)^2 - (\epsilon^+ - \epsilon_1)^2}. \quad (26)$$

This equation is also equivalent to that given by James.<sup>2</sup> Equation (26) will be applied without approximation to the functional form of the cross section.

Cross sections were computed with the Brysk and Zerby<sup>7</sup> relativistic photoelectric cross section program. This program was designed to use Dirac-Slater relativistic wavefunctions.<sup>8</sup> The actual wavefunctions used were computed with the Kohn-Sham<sup>9</sup> potential, i.e.,  $2/3$  of the Slater<sup>10</sup>  $[\rho(\mathbf{r})]^{1/3}$  exchange potential. In addition, experimental energy levels<sup>11</sup> were used rather than the computed Dirac-Slater eigenvalues. Equation (26) was then numerically integrated by the Gauss-Legendre method.

Equation (26) must first be transformed into a form convenient for calculation. When atomic units with  $\hbar = e = m = 1$  and  $c = 137.0367$  are used, and the integration variable  $\epsilon^+$  is redefined by subtracting  $mc^2$ , Eq. (26) may be rewritten as

$$f^+ = \left( \int_0^{\infty} \frac{\sigma(\epsilon^+ - \epsilon_1) (\epsilon^+ - \epsilon_1)^2 - \sigma(\hbar\omega) (\hbar\omega)^2}{(\hbar\omega)^2 - (\epsilon^+ - \epsilon_1)^2} d\epsilon^+ + P \int_0^{\infty} \frac{\sigma(\hbar\omega) (\hbar\omega)^2}{(\hbar\omega)^2 - (\epsilon^+ - \epsilon_1)^2} d\epsilon^+ \right) \frac{c}{2\pi^2}. \quad (27)$$

The first integral in Eq. (27) is now continuous at the former singularity, and the second integral is easily evaluated as

$$P \int_0^{\infty} \frac{\sigma(\hbar\omega) (\hbar\omega)^2}{(\hbar\omega)^2 - (\epsilon^+ - \epsilon_1)^2} d\epsilon^+ = \frac{1}{2} [ - (\hbar\omega) \sigma(\hbar\omega) ] \log \frac{|\hbar\omega - \epsilon_1|}{|\hbar\omega + \epsilon_1|}. \quad (28)$$

In order to perform the Gauss-Legendre numerical integration, the integration limits must be changed from 0 to  $\infty$  to 0 to 1 by making one of the following changes of variable:

$$x = -\epsilon_1 / (\epsilon^+ - \epsilon_1) \quad \text{for } 1 < \epsilon_1 < 70 \text{ keV}, \quad (29a)$$

$$x = [ -\epsilon_1 / (\epsilon^+ - \epsilon_1) ]^2 \quad \text{for } \epsilon_1 \geq 70 \text{ keV}, \quad (29b)$$

or

$$x = [ -\epsilon_1 / (\epsilon^+ - \epsilon_1) ]^{1/2} \quad \text{for } \epsilon_1 \leq 1 \text{ keV}. \quad (29c)$$

Substitution (29b) serves to contract the range of energies at which the cross sections must be calculated and substitution (29c) expands this range. These substitutions result in

$$f^+ = \frac{c\epsilon_1}{2\pi^2} \int_0^1 \frac{\sigma(-\epsilon_1/x) \cdot \epsilon_1^2 - \sigma(\hbar\omega) (\hbar\omega)^2 x^2}{x^2 [x^2 (\hbar\omega)^2 - \epsilon_1^2]} dx + \text{Eq. (28)}, \quad (30a)$$

$$f^+ = - \frac{c}{4\pi^2} \epsilon_1 \int_0^1 \frac{\sigma(-\epsilon_1 x^{1/2}) \cdot \epsilon_1^2}{x^{1/2} [(\hbar\omega x)^2 - \epsilon_1^2 x]} dx + \text{Eq. (28)}, \quad (30b)$$

$[\sigma(\hbar\omega) = 0 \text{ in this case for x rays of interest}]$ ,

$$f^+ = \frac{-c\epsilon_1}{\pi^2} \int_0^1 \frac{\sigma(-\epsilon_1/x^2) \epsilon_1^2 - \sigma(\hbar\omega) (\hbar\omega)^2 x^4}{x^3 [(\hbar\omega)^2 x^4 - \epsilon_1^2]} dx + \text{Eq. (28)}. \quad (30c)$$

The term in Eq. (28) must be added to Eq. (30). With these substitutions it was found that a five-point numerical integration gave  $f^+$  with a numerical accuracy of about four significant figures. The total real dispersion,  $\Delta f'$ , is then given by  $f^+$  and the energy term of Eq. (19).

### III. RESULTS

In addition to the cross sections at the five energies selected by the Gauss-Legendre integration method, the cross section at the incident x-ray energy must also be calculated. The dispersion terms  $\Delta f'$  and  $\Delta f''$  were calculated in the above fashion for the  $K_{\alpha 1}$  energies of Cr, Fe, Cu, Mo, and Ag. The results are given

in Table I. The total cross sections were converted to mass absorption coefficients and these values are also listed in Table I. Table II lists the energy dependent terms of Eq. (19).

The dispersion terms in Table I are for the wavelengths commonly used in crystallography. For other wavelengths the cross sections at those wavelengths must be known. One can interpolate with sufficient

TABLE I. Anomalous scattering factors and mass absorption coefficients (in square centimeters per gram).

ATOM	CR K ALPHA 1 2.28962A			FE K ALPHA 1 1.93597A			CU K ALPHA 1 1.54052A			MO K ALPHA 1 .70926A			AG K ALPHA 1 .55936A		
	FP	FPP	MU/RHO	FP	FPP	MU/RHO	FP	FPP	MU/RHO	FP	FPP	MU/RHO	FP	FPP	MU/RHO
LI	.002	.001	.9	.002	.001	.5	.001	.000	.3	-.007	.000	.0	-.000	.000	.0
BE	.008	.003	2.9	.005	.002	1.7	.003	.001	.8	-.000	.000	.1	-.001	.000	.0
B	.018	.009	6.8	.013	.007	4.0	.008	.004	1.9	.000	.001	.2	-.000	.000	.1
C	.035	.021	13.8	.026	.015	8.1	.017	.009	3.9	.002	.002	.3	.000	.001	.1
N	.059	.042	23.1	.044	.029	13.7	.029	.018	6.7	.004	.003	.6	.001	.002	.3
O	.090	.073	35.5	.069	.052	21.3	.047	.032	10.5	.008	.006	.9	.003	.004	.4
F	.129	.119	48.9	.100	.085	29.5	.069	.053	14.7	.014	.010	1.3	.006	.006	.6
NE	.174	.184	70.9	.138	.132	43.0	.097	.083	21.6	.021	.016	2.0	.011	.010	.9
NA	.223	.270	91.4	.180	.195	55.8	.129	.124	28.2	.030	.025	2.6	.016	.015	1.2
MG	.272	.381	122.0	.224	.277	74.8	.165	.177	38.1	.042	.036	3.6	.023	.022	1.7
AL	.318	.522	150.4	.269	.381	92.8	.204	.246	47.6	.056	.052	4.6	.032	.031	2.2
SI	.355	.693	191.9	.311	.509	119.1	.244	.330	61.5	.072	.071	6.1	.042	.043	2.9
P	.377	.900	225.9	.347	.664	140.8	.283	.434	73.2	.090	.095	7.3	.055	.058	3.6
S	.374	1.142	276.9	.370	.847	173.6	.319	.557	90.8	.110	.124	9.3	.068	.076	4.5
CL	.335	1.423	312.0	.375	1.061	196.6	.348	.702	103.6	.132	.159	10.8	.084	.099	5.3
AR	.243	1.747	340.0	.352	1.309	215.4	.366	.872	114.2	.155	.201	12.1	.101	.125	5.9
CA	.070	2.110	419.5	.286	1.589	267.2	.365	1.066	142.6	.179	.250	15.4	.118	.156	7.6
K	-.221	2.514	487.6	.163	1.904	312.3	.341	1.286	167.8	.203	.336	18.4	.137	.193	9.1
SC	-.717	2.968	513.3	-.038	2.256	329.9	.285	1.533	178.4	.226	.372	19.9	.156	.235	9.9
TI	-1.683	3.470	563.1	-.357	2.643	362.8	.189	1.807	197.3	.248	.446	22.4	.175	.283	11.2
V	-3.861	.459	70.0	-.884	3.070	396.1	.035	2.110	216.6	.287	.530	25.1	.194	.338	12.6
CR	-2.161	.548	82.0	-1.793	3.533	446.6	-.198	2.443	245.8	.284	.624	28.9	.213	.399	14.6
MN	-1.639	.650	92.0	-3.367	.481	57.5	-.568	2.808	267.3	.295	.729	32.0	.229	.468	16.2
FE	-1.339	.764	106.4	-2.095	.566	66.6	-1.179	3.204	300.1	.301	.845	36.5	.244	.565	18.5
CO	-1.124	.893	117.7	-1.623	.662	73.8	-2.464	3.608	320.3	.299	.973	39.8	.256	.630	25.3
NI	-.956	1.036	137.2	-1.343	.769	86.1	-2.956	.509	45.4	.285	1.113	45.6	.261	.724	23.4
CU	-.795	1.196	146.3	-1.129	.888	91.9	-2.019	.589	48.5	.263	1.266	48.0	.265	.826	24.7
ZN	-.684	1.373	163.3	-.978	1.021	102.7	-1.612	.678	54.3	.222	1.431	52.7	.260	.938	27.3
GA	-.570	1.569	175.0	-.841	1.168	110.1	-1.354	.777	58.3	.163	1.609	55.6	.249	1.059	28.9
GE	-.462	1.786	191.3	-.717	1.331	120.5	-1.163	.886	63.9	.081	1.801	59.8	.228	1.190	31.1
AS	-.365	2.022	209.8	-.607	1.508	132.3	-1.011	1.006	70.2	-.030	2.007	64.5	.196	1.332	33.8
SE	-.273	2.283	224.7	-.503	1.704	141.9	-.879	1.139	75.5	-.178	2.223	67.8	.152	1.481	35.6
BR	-.198	2.563	249.3	-.413	1.916	157.6	-.767	1.283	84.0	-.374	2.456	74.0	.090	1.643	39.0
KR	-.130	2.872	266.4	-.328	2.149	168.6	-.665	1.439	89.8	-.652	2.713	78.0	.008	1.820	41.7
RR	-.082	3.201	291.1	-.256	2.398	184.5	-.574	1.638	98.4	-1.744	2.973	83.8	-.099	2.033	44.5
SR	-.012	3.608	320.1	-.161	2.709	203.2	-.465	1.820	108.7	-1.657	3.264	89.7	-.230	2.203	47.8
Y	.006	4.002	349.9	-.106	3.009	222.4	-.386	2.225	119.1	-2.951	3.542	95.9	-.406	2.411	51.5
ZR	.007	4.422	376.9	-.061	3.329	239.9	-.314	2.245	128.7	-2.965	.560	14.8	-.639	2.630	54.8
NB	.013	4.876	408.0	-.028	3.676	260.1	-.248	2.482	139.8	-2.197	.621	16.1	-.957	2.860	56.5
MO	.063	5.353	433.7	-.012	4.043	277.0	-.191	2.735	149.1	-1.825	.688	17.3	-1.416	3.103	61.4
TC	.153	5.862	460.3	-.017	4.434	294.4	-.145	3.005	158.8	-1.590	.759	18.5	-2.205	3.353	64.3
RU	.270	6.406	492.8	-.039	4.854	315.7	-.105	3.296	170.6	-1.420	.836	19.9	-5.524	3.651	68.6
RH	.424	6.984	527.6	-.083	5.300	338.5	-.077	3.605	183.2	-1.287	.919	21.5	-2.649	.596	11.0
PD	.639	7.594	554.9	-.157	5.773	356.6	-.059	3.934	193.4	-1.177	1.007	22.8	-2.128	.654	11.7
AG	.924	8.235	593.5	-.259	6.271	382.1	-.060	4.282	207.6	-1.885	1.131	24.6	-1.834	.717	12.6
CD	1.303	8.912	616.4	-.416	6.800	397.7	-.079	4.653	216.6	-1.005	1.202	25.8	-1.637	.783	13.2
IN	1.788	9.627	651.8	-.626	7.356	421.1	-.126	5.245	229.8	-.936	1.310	27.5	-1.493	.854	14.1
SN	2.401	10.380	679.9	-.888	7.943	439.9	-.194	5.459	240.6	-.873	1.424	28.9	-1.378	.930	14.9
SB	-3.194	11.166	713.0	-1.214	8.557	462.0	-.287	5.894	253.2	-.616	1.546	30.6	-1.284	1.010	15.6
TE	-4.267	11.995	730.8	-1.630	9.203	474.1	-.418	6.352	260.4	-.772	1.675	31.6	-1.212	1.096	16.3
I	-5.852	12.850	787.2	-2.147	9.885	512.0	-.579	6.835	281.7	-.726	1.812	34.4	-1.144	1.178	17.8
XE	-8.133	11.933	706.5	-2.812	10.608	531.1	-.783	7.348	292.7	-.684	1.958	35.9	-1.084	1.284	18.6
CS	-10.742	12.919	755.7	-3.652	11.302	563.0	-1.022	7.904	311.1	-.644	2.119	38.4	-1.029	1.391	19.9
BA	-11.460	9.981	565.0	-4.832	12.164	582.2	-1.334	8.460	322.2	-.613	2.282	40.0	-.983	1.500	22.7
LA	-12.135	3.565	199.5	-6.683	12.937	612.2	-1.716	9.036	340.2	-.588	2.452	42.5	-.942	1.615	22.1
CE	-9.574	3.843	213.2	-8.388	11.953	560.8	-2.170	9.648	360.2	-.564	2.632	45.2	-.904	1.735	23.5
PR	-7.817	4.130	227.9	-12.457	6.285	293.2	-2.939	10.535	391.1	-.530	2.845	48.6	-.859	1.873	25.2
ND	-7.486	4.427	238.6	-11.016	9.874	450.0	-3.431	10.933	396.5	-.535	3.018	50.4	-.842	1.995	26.3
PM	-6.891	4.741	250.7	-12.122	3.627	162.2	-4.357	11.614	413.3	-.530	3.225	52.8	-.818	2.135	27.6
SM	-6.429	5.073	262.3	-9.616	3.883	169.8	-5.696	12.320	428.6	-.533	3.442	55.1	-.798	2.281	28.8
EU	-6.050	5.416	277.1	-8.352	4.149	179.5	-7.718	11.276	388.1	-.542	3.669	58.1	-.782	2.435	30.4
GD	-5.779	5.773	285.4	-7.565	4.427	185.0	-9.242	11.466	397.4	-.564	3.904	59.8	-.774	2.595	31.3
DY	-5.525	6.153	301.0	-6.980	4.721	195.3	-9.498	9.242	304.2	-.591	4.151	62.9	-.767	2.764	33.0
HO	-5.250	6.549	313.3	-6.492	5.026	203.3	-10.423	9.748	313.8	-.619	4.410	65.4	-.761	2.940	34.4
ER	-5.040	6.958	328.0	-6.112	5.343	213.0	-12.255	3.704	117.5	-.666	4.678	68.3	-.765	3.124	36.0
HR	-4.878	7.387	343.3	-5.810	5.675	223.0	-9.733	3.937	123.1	-.723	4.958	71.4	-.773	3.318	37.6
FM	-4.753	7.833	360.5	-5.565	6.022	234.3	-8.488	4.181	129.5	-.795	5.248	74.8	-.790	3.515	39.5
YB	-4.652	8.291	372.5	-5.361	6.378	242.3	-7.701	4.432	134.0	-.884	5.548	77.2	-.815	3.723	40.9
LU	-4.580	8.759	389.2	-5.190	6.745	253.4	-7.133	4.693	140.3	-.988	5.858	80.6	-.847	3.937	42.7
HT	-4.592	9.277	404.1	-5.088	7.148	263.3	-6.715	4.977	145.8	-1.118	6.185	83.5	-.890	4.164	44.3
TA	-4.540	9.811	421.5	-4.948	7.565	274.8	-6.351	5.271	152.4	-1.258	6.523	86.8	-.937	4.399	46.2
W	-4.499	10.364	438.2	-4.823	7.996	285.9	-6.048	5.577	158.7	-1.421	6.872	90.0	-.993	4.643	48.0
RE	-4.483	10.929	456.3	-4.719	8.439	297.9	-5.790	5.891	165.5	-1.598	7.232	93.5	-1.048	4.894	49.9
OS	-4.503	11.520	470.9	-4.647	8.903	307.7	-5.581	6.221	171.1	-1.616	7.605	96.3	-1.127	5.156	51.5
IR	-4.527	12.140	491.0	-4.578	9.389	321.1	-5.391	6.566	178.7	-2.066	7.990	100.1	-1.216	5.427	53.6
PT	-4.584	12.787	509.5	-4.535	9.895	333.4	-5.233	6.925	185.7	-2.352	8.388	103.5	-1.319	5.708	55.6
AU	-4.668	13.451	530.9	-4.510	10.418	347.7	-5.096	7.297	193.8	-2.688	8.798	107.6	-1.438	5.998	57.8
HG	-4.803	14.143	548.1	-4.523	10.963	359.2	-4.990	7.686	200.4	-3.084	9.223	110.7	-1.576	6.299	59.6
TL	-4.945	14.860	565.3	-4.532	11.528	370.8	-4.883	8.089	207.0	-3.556	9.659	113.8	-1.730	6.610	61.4
PB	-5.161														

TABLE II. Calculated values of  $5/3 (E_{\text{tot}}/mc^2)$ .

LI	-.001	BR	-.231	HO	-1.119
BE	-.001	KR	-.247	ER	-1.161
B	-.002	RB	-.264	TM	-1.204
C	-.003	SR	-.282	YB	-1.248
N	-.005	Y	-.300	LU	-1.293
O	-.007	ZR	-.319	HF	-1.338
F	-.009	NB	-.338	TA	-1.385
NE	-.011	MO	-.359	W	-1.433
NA	-.014	TC	-.380	RE	-1.482
MG	-.018	RU	-.401	OS	-1.532
AL	-.021	RH	-.424	IR	-1.583
SI	-.026	PD	-.447	PT	-1.636
P	-.030	AG	-.471	AU	-1.689
S	-.035	CD	-.496	HG	-1.743
CL	-.041	IN	-.521	TL	-1.799
AR	-.047	SN	-.547	PB	-1.856
K	-.053	SB	-.575	BI	-1.914
CA	-.060	TE	-.602	PO	-1.973
SC	-.068	I	-.631	AT	-2.033
TI	-.075	XE	-.660	RN	-2.095
V	-.084	CS	-.690	FR	-2.157
CR	-.093	BA	-.721	RA	-2.221
MN	-.102	LA	-.753	AC	-2.287
FE	-.113	CE	-.786	TH	-2.353
CO	-.123	PR	-.819	PA	-2.421
NI	-.135	ND	-.854	U	-2.490
CU	-.146	PM	-.889	NP	-2.561
ZN	-.159	SM	-.925	PU	-2.633
GA	-.172	EU	-.962	AM	-2.707
GE	-.186	GD	-1.000	CM	-2.782
AS	-.200	TB	-1.039	BK	-2.858
SE	-.215	CY	-1.079	CF	-2.936

accuracy from the cross sections that have already been computed. We are separately publishing a Los Alamos Scientific Laboratory report<sup>12</sup> containing all of the necessary cross sections and energies and a Fortran program which interpolates the cross section for the desired incident radiation and computes the dispersion. This report is available from the authors on request.

#### IV. DISCUSSION

The present results are not greatly different from those given by Cromer<sup>1</sup> but should be more accurate because of the more rigorous treatment.<sup>13</sup> Much of the difference is related to the fact that the cross section-vs-energy relation is not as simple as indicated in Eq. (1). Figure 1 shows log-log plots of calculated cross section vs energy for some of the xenon orbitals. The dashed lines are the cross sections given by Eq. (1), with the cross section at the edge computed from the oscillator strength<sup>1</sup> and an exponent of  $7/3$  for the  $2s$  orbital and  $5/2$  for the other orbitals shown.

An estimate of the contribution of unoccupied bound states for the  $1s\ 1/2$  orbital of uranium was made in two ways. First, in the self-consistent atomic calculation, the potential was changed to go to zero at a finite radius rather than as  $1/r$ . This change has the

effect of pushing many of the formerly unoccupied bound states into the continuum. The cross-section calculations hardly changed. One can also formally treat these transitions as a sum, analogous to the  $f^+$  integral and write;

Unoccupied bound state contribution to

$$f^+ = \sum_i \{g(i, k) (\epsilon_i - \epsilon_k)^2 / [(\hbar\omega)^2 - (\epsilon_i - \epsilon_k)^2]\} \\ = \{\Delta E^2 / [(\hbar\omega)^2 - \Delta E^2]\} \sum_i g(i, k), \quad (31)$$

where the  $g(i, k)$  are the transition probability matrix elements used in the sum rule, and  $\epsilon_i$  is the energy of an unoccupied bound state. Because the  $\epsilon_i$  are virtually the same,  $(\epsilon_i - \epsilon_k)$  can be treated as a constant,  $\Delta E$ . The wavefunctions were computed for these states up to  $10p\ 3/2$ , beyond which the program would not bind an electron, and the matrix elements were computed. The results are given in Table III. It is clear that neglect of these transitions has produced little error in  $f^+$ .

#### V. COMPARISON WITH EXPERIMENT

Experimental measurement of  $\Delta f'$  or  $\Delta f''$  is very difficult. For  $\Delta f'$ , intensity measurements must be made on an absolute scale and the unmodified scattering factor,  $f_0$ , must be known. In principle,  $\Delta f''$  can be determined from the absorption coefficient, but it is difficult to separate the true photoelectric absorption from all other processes that diminish the intensity. The best way to measure  $\Delta f''$  seems to be the very direct process of measuring diffracted intensities of Friedel related pairs, i.e.,  $I(hkl)$  and  $I(\bar{h}\bar{k}\bar{l})$ , from suitable noncentric crystals.

Zachariasen has made direct measurements of  $\Delta f''$  for Si,<sup>14</sup> K,<sup>15</sup> and P.<sup>15</sup> His results and the present and former calculations are given in Table IV. The present calculations are in much better agreement with experiment.

Grimvall and Persson<sup>16</sup> have recently published experimental work on absorption by the  $1s\ 1/2$  orbital of germanium. They made experimental estimates of  $\Delta f'$ ,

TABLE III. Contribution of unoccupied bound states to  $f^+$  for the  $1s\ 1/2$  orbital of uranium.

Transition	$f^+$ (Cu radiation)
$1s\ 1/2 \rightarrow 7p\ 1/2$	$-6.2 \times 10^{-6}$
$7p\ 3/2$	$-1.3 \times 10^{-6}$
$8p\ 1/2$	$-1.6 \times 10^{-6}$
$8p\ 3/2$	$-4.2 \times 10^{-6}$
$9p\ 1/2$	$-6.8 \times 10^{-7}$
$9p\ 3/2$	$-1.9 \times 10^{-6}$
$10p\ 1/2$	$-4.3 \times 10^{-7}$
$10p\ 3/2$	$-1.4 \times 10^{-6}$
	$-29.4 \times 10^{-6}$

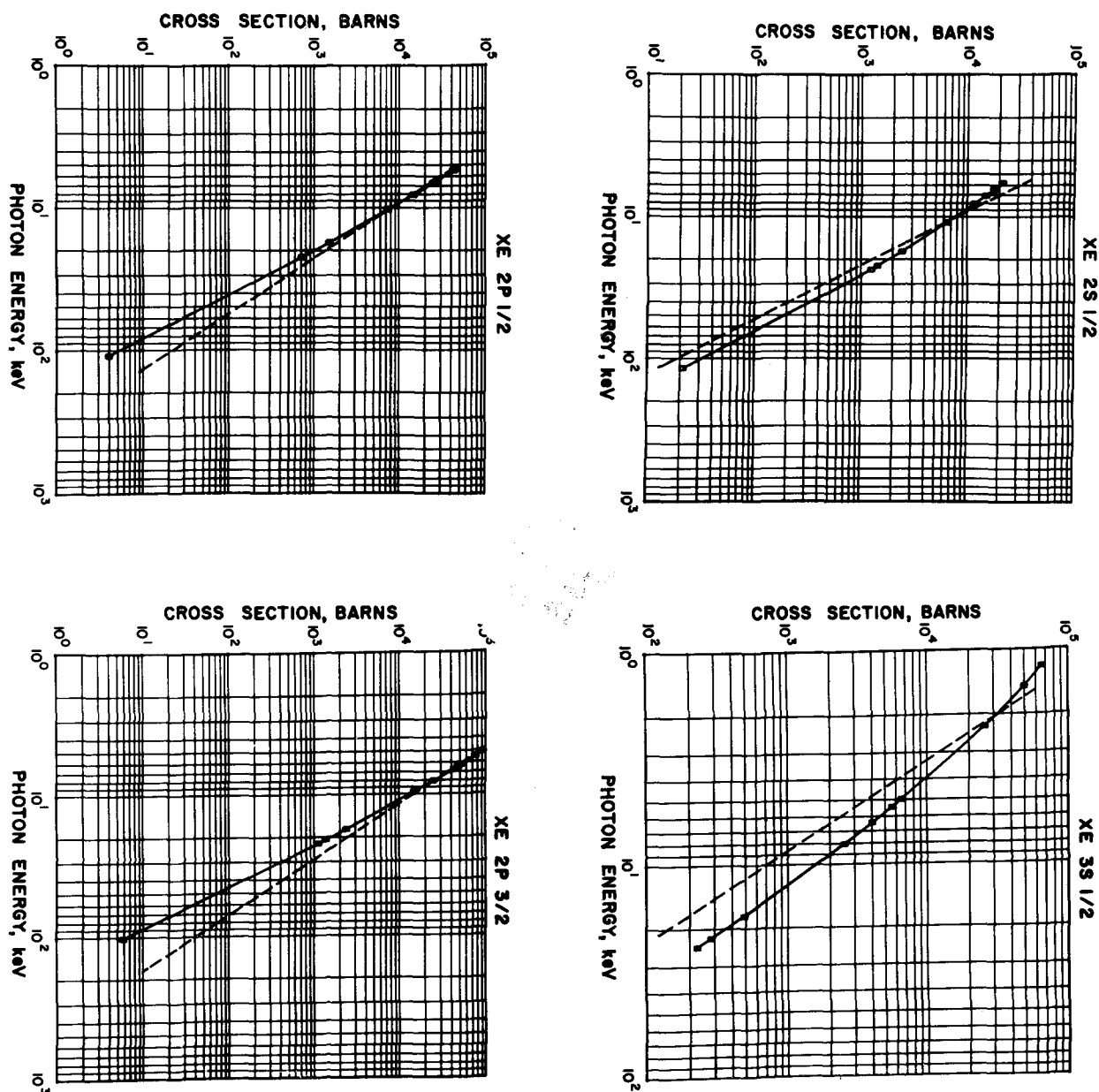


FIG. 1. Calculated cross sections vs photon energy for several xenon orbitals. The dashed lines are the curves calculated from Eq. (1).

TABLE IV. Comparison of experimental<sup>14,15</sup> and calculated  $\Delta f''$  for Si, P, and K.

	Cu $K_\alpha$			Mo $K_\alpha$		
	Exptl	Present	Cromer <sup>1</sup>	Exptl	Present	Cromer
Si	$0.31 \pm 0.01$	0.330	0.36		0.071	0.09
P	$0.44 \pm 0.02$	0.434	0.46	$0.107 \pm 0.007$	0.095	0.12
K	$1.04 \pm 0.06$	1.066	1.11	$0.271 \pm 0.010$	0.250	0.30



TABLE V. Comparison of experimental<sup>16</sup> and calculated  $\Delta f'$  and  $\Delta f''$  for the  $1s\ 1/2$  orbital of germanium.

Radiation	$\Delta f'$			$\Delta f''$		
	Exptl	Present	Cromer <sup>1</sup>	Exptl	Present	Cromer
Cu $K_\alpha$	-1.79	-1.803	-1.78	0	0	0
Mo $K_\alpha$	0.08	-0.082	0.01	1.58	1.588	1.60
Ag $K_\alpha$	0.27	-0.142	0.21	1.06	1.054	1.05

TABLE VI. Comparison of experimental<sup>18</sup> and calculated  $\Delta f'$  and  $\Delta f''$  for the rare gases with Mo  $K_\alpha$  radiation.

	$\Delta f'$			$\Delta f''$		
	Exptl	Present	Cromer <sup>1</sup>	Exptl	Present	Cromer
Ne	-0.01	0.021	0.03	$0.017 \pm 0.004$	0.016	0.02
Ar	0.10	0.155	0.18	$0.202 \pm 0.005$	0.201	0.24
Kr	-0.81	-0.652	-0.47	$2.78 \pm 0.07$	2.713	2.96
Xe	-0.40	-0.684	-0.59	$2.09 \pm 0.01$	1.958	2.30

$\Delta f''$ ,  $g$ , and the exponent in the empirical formula of Eq. (1). By extrapolating the absorption curve from energies that the  $K$  edge did not absorb, they were able to estimate the absorption from the  $K$  edge alone. Table V gives a comparison of their results with calculated values. The agreement for  $\Delta f''$  is good but for  $\Delta f'$ , except for Cu radiation, is not as good as one would like. Grimvall and Persson obtained  $\Delta f'$  from their absorption data by forcing it to fit Eq. (1), which has been shown by these calculations to be an inadequate approximation. It would be interesting to fit their data to a two-term function of the form of Eq. (1) and then compute the  $\Delta f'$  integral. Their absorption data were only given graphically, so we could not do this calculation. The calculated  $\Delta f'$  includes a contribution of  $-0.088$  from the single orbital equivalent of Eq. (19). This kinetic energy of a single electron was not available as output from our relativistic atomic calculations. Instead, it was estimated from Hartree calculations by Larson and Waber.<sup>17</sup>

The best measurement of  $\Delta f'$  appears to be that of Chipman and Jennings<sup>18</sup> on the rare gases. Table VI gives a comparison of their results with calculated values. The agreement with experiment is improved over previous values in all cases except  $\Delta f'$  for xenon.

## VI. CONCLUSION

We believe that the present results for both  $\Delta f'$  and  $\Delta f''$  are significantly improved over those of previous calculations. The fact that  $\Delta f''$  now agrees better with experiment shows that the cross-section calculations are reasonably good, and because a more rigorous treatment of the cross sections to obtain  $\Delta f'$  has been used, these values should also be more accurate. Much further experimental work on both these quantities, however, is very desirable.

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