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Incoherent X-ray Scattering in the Free-Fermi-Gas Approach

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A simple equation is derived from one- and two-particle density matrices in the free-Fermi-gas approximation for obtaining the incoherent intensity of X-rays scattered by an atomic N-electron system. The accuracy of the equation is tested on the Thomas–Fermi–Dirac statistical atomic model. The numerical results are compared with those obtained from the known Heisenberg–Bewilogua function and with the atomic incoherent intensities calculated by D. T. Cromer [*J. Chem. Phys.* (1967). **47**, 1892–1893; (1969). **50**, 4857–4859] using complete Waller–Hartree theory and the HF SCF model. The results obtained by the present method from the TFD model are in good agreement with Cromer's data.

1. Introduction

Incoherent scattering functions of X-rays are known for all the atoms and a limited number of ions ($Z \leq 32$) from the works of several authors (Freeman, 1959, 1960; Freeman & Watson, 1962; Cromer, 1967, 1969; Tavard, Nicolas & Rouault, 1967; Pohler & Hanson, 1965). The majority of these works were based on the complete Waller & Hartree (1929) (WH) theory. The calculations differ from each other in the use of either numerical or analytical, HF or HFS SCF wave functions, respectively.

Owing to the complexity of numerical calculations, the incoherent intensities of heavy atoms based on the WH theory, were determined only in the late sixties (Cromer, 1967, 1969). A simplification of the WH theory is achieved by neglecting the exchange effect. It was James & Brindley (1931) who determined incoherent scattering functions on this way which, however, resulted in significant errors.

For the atomic incoherent intensities, an approximation based on the statistical TF atomic model, was performed by Heisenberg (1931). The resulting universal function was numerically evaluated by Bewilogua (1931) (HB function), and later by Pohler & Hanson (1965). The determination of the incoherent scattering functions from the universal HB function for atoms with different atomic numbers reduces to a task of scaling, the atomic number Z figuring in the argument w of the HB function. Scattering functions more exact than these for the heavy atoms have been failing up to 1967. It is worth mentioning that whereas coherent scattering functions have been determined on the basis of nearly all the improved statistical atomic models (Thomas & Umeda, 1957; Csavinszky, 1970; Dobay-Szegleth, 1970; Bonham & Strand, 1963), this work has not been done for the incoherent ones with the sole exception of the TF model.

In the present paper a simple relationship is shown, in the free-Fermi-gas approach, between the incoherent scattering function on one part, and the electron density and the total electrostatic potential of an N-electron system on the other. With the aid of this relationship, atomic incoherent scattering functions were determined on the basis of TF and TFD atomic models respectively.

The results are compared to the values obtained from the HB function which is based on Heisenberg's equation, and to those given by Cromer (1967, 1969) who used the WH theory and HF SCF wave functions. A good agreement was found between the latter and those computed from the TFD model by the present author.

Incoherent scattering functions of the ions are known in the range of lower atomic numbers only ($Z < 32$). The relationship presented below lends itself to calculating the incoherent scattering functions of heavy ions in a simple way. The knowledge of the incoherent intensities of the ions is particularly important in structural studies of electrolyte solutions by X-ray diffraction. In the majority of works on this subject, the incoherent intensities of the heavy ions are approximated by the values of Bewilogua's function for the isoelectronic atom (Wertz & Kruh, 1970). In some other papers the HF incoherent values of the isoelectronic atom are used for high values of the scattering variable, and the function is extrapolated to zero on an arbitrary way in the range of small scattering-variable values (Bol, Gerrits & van Pantheleon van Eck, 1970).

2. Theory

2.1 *Waller–Hartree approximation*

For the total intensity of X-ray photons scattered by an N-electron system at a scattering angle θ – provided that the energy of the primary photon is higher than the energy differences between the bound states of the system – the Waller–Hartree theory gives the following expression (Benesch & Smith, 1970)

$$I_t(\theta)/I_{\rm cl} = \langle \psi_g | PP^* | \psi_g \rangle \quad (1)$$

where ψ_g is the normalized N-electron wave function of the system in ground state, $I_{\rm cl}$ the total intensity of photons scattered on a classical point charge. Scattering operator P is defined as

$$P=\sum_{j=1}^{N}\exp\{i\mathbf{q}\mathbf{r}_j\}\,, \tag{2}$$

scattering vector $\mathbf{q}$ representing the difference between the wave-number vectors of the primary and scattered photons,

$$|\mathbf{q}|=(4\pi/\lambda)\sin(\theta/2)=4\pi s=q\,.$$

The contribution of the coherently scattered X-ray photons to the total intensity is

$$I_c(\theta)/I_{\rm cl}=|\langle\psi_g|P|\psi_g\rangle|\,. \tag{3}$$

Using the following definitions for one-particle and two-particle density matrices (Löwdin, 1959)

$$\gamma(1'|1)=\frac{2}{N-1}\int\Gamma(1',2'|1,2)\mathrm{d}2\,, \tag{4}$$

and

$$\Gamma(1'2'|1,2)=\tbinom{N}{2}\int\psi_g(1',2',3\ldots N)\psi_g^*(1,2,3\ldots N)\times\mathrm{d}3\mathrm{d}N$$

respectively, where symbol 1 denotes the space and spin coordinates of the particle: $1=(\mathbf{r},\sigma)$, and integration includes spin summation. Expression (1) for the total intensity can be transcribed (Benesch & Smith, 1970) into

$$I_t(\mathbf{q})/I_{\rm cl}=N+2\int\exp\{i\mathbf{q}(\mathbf{r}_1-\mathbf{r}_2)\}\Gamma(1',2'|1,2)\mathrm{d}1\mathrm{d}2 \tag{5}$$

whereas the coherent component can be expressed with the one-particle density matrix as

$$I_c(\mathbf{q})/I_{\rm cl}=|\int\exp\{i\mathbf{q}\mathbf{r}\}\gamma(1'|1)\mathrm{d}1|^2. \tag{6}$$

From (5) and (6) it is evident that the total intensity component is a two-particle property whereas the coherent scattering is a one-particle property.

If the N-electron wave function ψ_g is approximated by the normalized Slater determinant of the one-electron state spin orbitals $\varphi_k(1)$ (HF approximation) according to

$$\psi_g=\frac{1}{(N!)^{1/2}}\det\{\varphi_k(1_i)\}\,, \tag{7}$$

then one-particle and two-particle matrices take the following forms:

$$\gamma(1'|2)=\sum_{k=1}^{N}\varphi_k^*(1')\varphi_k(2) \tag{8}$$

and

$$\Gamma(1',2')|1,2)=\tfrac{1}{2}\begin{vmatrix}\gamma(1'|1) & \gamma(1'|2)\\ \gamma(2'|1) & \gamma(2'|2)\end{vmatrix}$$

respectively.

The second relationship, *i.e.* the fact that the two-particle density matrix is defined by the one-particle matrices is characteristic of the HF approach. Benesch & Smith (1970) have pointed out that equation (5) for the total intensity is equivalent to the total intensity expression of the WH theory

$$I_t(s)/I_{\rm cl}=|\sum_j f_{jj}|^2+N-\sum_j|f_{jj}|^2-\sum_j\sum_{k\neq j}|f_{jk}|^2 \tag{9}$$

where

$$f_{jk}=\int\exp\{i\mathbf{q}\mathbf{r}\}\varphi_k(\mathbf{r})\varphi_j^*(\mathbf{r})\mathrm{d}\mathbf{r}\delta(\sigma_j,\sigma_k)\,. \tag{10}$$

The first term of the right-hand side of (9) is the coherent intensity component. The last one arises from the antisymmetry of the HF N-electron wave function. This antisymmetry leads to the exchange correlation between electrons of identical spin which is called the 'Fermi hole'.

If the N-electron wave function is approximated by the Hartree product of one-electron spin orbitals, the last term in (9) cancels out.

2.2 *Fermi-gas approximation*

Expression (6) for the total intensity is presented below in the Fermi-gas approach. Let us suppose that the temperature of the electron gas is zero, *i.e.* each of the $N/2$ energetically deepest cells of the phase space is occupied by 2 electrons with antiparallel spins and the other cells are empty.

The N-electron wave function is approximated by a Slater determinant composed of one-electron spin orbitals of the form

$$\varphi_j(1_i)=\frac{1}{(\Omega)^{1/2}}\exp\{i\mathbf{k}_j\mathbf{r}_i\}\alpha(\sigma_j)\,.$$

According to this, the spin-independent one-particle density matrix can be written in the form (McWeeny, 1960)

$$\gamma(\mathbf{r}_1|\mathbf{r}_2)=\frac{2}{(2\pi)^3}\int_{k\leq k_f}\exp\{-i\mathbf{k}(\mathbf{r}_1-\mathbf{r}_2)\}\mathrm{d}\mathbf{k}\,, \tag{12}$$

k_f denoting the Fermi wave number.

With this expression, the corresponding two-particle density matrix from (8) takes the form

$$2\Gamma(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)=\frac{k_f^3}{3\pi^2}\,\frac{k_f^3}{3\pi^2}-\frac{1}{32\pi^6}\int_{k\leq k_f}\exp\{-i\mathbf{k}(\mathbf{r}_1-\mathbf{r}_2)\}\mathrm{d}\mathbf{k}\times\int_{k'\leq k_f}\exp\{i\mathbf{k}'(\mathbf{r}_1-\mathbf{r}_2)\}\mathrm{d}\mathbf{k}'\,. \tag{13}$$

By making use of the relationship between the maximal wave number and the electron density of a Fermi-gas according to

$$k_f^3(r)=3\pi^2\varrho(r)\,, \tag{14}$$

we obtain from (6) for the intensity of coherently scattered photons the expression

$$I_c(s)/I_{\mathrm{cl}} = f(s) * f(s)$$

and

$$f(s) = \int \exp\{i\mathbf{q}\mathbf{r}\}\varrho(r)\mathrm{d}(\mathbf{r})\,. \tag{15}$$

So it can be seen that the coherent intensity component is determined by the Fourier transform of the electron density in this Fermi-gas approach also. The incoherent part of the total intensity from (13) and (5) is

$$\begin{aligned} I_i(s)/I_{\mathrm{cl}} = N - \frac{1}{32\pi^6}\int &\exp\{i\mathbf{q}(\mathbf{r}_1-\mathbf{r}_2)\} \\ &\times \int_{k\le k_f} \exp\{-i\mathbf{k}(\mathbf{r}_1-\mathbf{r}_2)\}\mathrm{d}\mathbf{k} \\ &\times \int \exp\{i\mathbf{k}'(\mathbf{r}_1-\mathbf{r}_2)\}\mathrm{d}\mathbf{k}'\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\,. \end{aligned} \tag{16}$$

If

$$\mathbf{r}' = \mathbf{r}_1 - \mathbf{r}_2$$

and integration over the relative coordinate is carried out, (16) is reduced to

$$I_i(s)/I_{\mathrm{cl}} = N - \frac{1}{4\pi^3}\int \mathrm{d}\mathbf{r} \iint_{k,k'\le k_f} \mathrm{d}\mathbf{k}\mathrm{d}\mathbf{k}'\delta(\mathbf{q}+\mathbf{k}'-\mathbf{k})\,. \tag{17}$$

The delta-function in the integrand represents the momentum conservation law

$$\mathbf{q} = \mathbf{k} - \mathbf{k}'\,. \tag{18}$$

We remark, however, that (18) is not quite correct for incoherent scattering since vector **q** is only the azimuthal component of the momentum transfer. In (18) the change of magnitude of the momentum, which is in any case characteristic of the incoherent scattering, is neglected. This neglect, however, is already implied in the WH theory, and thus also in equation (5).

It follows from the above that the sixfold integral over **k** figuring in (17) must be taken in the overlap range of two spheres, each of radius k_f and off-centred by a vector **q** from one another, (Fig. 1). The k_z axis of the coordinate system in the Figure is taken coincident with the scattering vector. From equation (18), and the condition $k,k' \le k_f$ follows, that

$$|\mathbf{q}| = |\mathbf{k}-\mathbf{k}'| \le 2k_f\,. \tag{19}$$

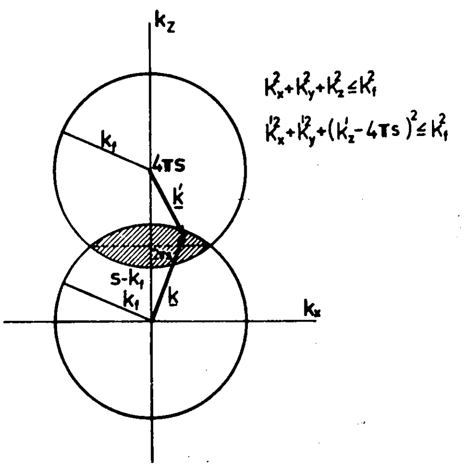

Fig. 1. Integration range of equation (19) in the k plane.

Contributions to the integral are furnished by only those electron states with momenta $\mathbf{p} = \hbar\mathbf{k}$ for which condition (18) is fulfilled, and the diameter $2k_f$ of the momentum sphere is not less than $4\pi s$, the modulus of the scattering-variable vector. In space these electron states are located within a sphere of radius r_0. The limiting radius r_0 is implicity defined by the following equation derived from (19) and (14)

$$2[3\pi^2\varrho(r_0)]^{1/3} - a_0 4\pi s = 0\,. \tag{20}$$

Taking into consideration all the above conditions and integrating over **k** in the range shown in Fig. 1 we obtain

$$\begin{aligned} I_i(s)/I_{\mathrm{cl}} = N - \frac{1}{4\pi^3}\int \mathrm{d}\mathbf{r}\,\Big[\int_{q-k_f}^{q/2} (k_f^2 - k_z^2 + 2k_z q - q^2)\mathrm{d}k_z \\ + \int_{q/2}^{k_f} (k_f^2 - k_z^2)\mathrm{d}k_z\Big] = \frac{4}{3\pi}\int_{r_0}^{\infty} r^2 k_f(r)\mathrm{d}r \\ + 4a_0 s\int_0^{r_0} k_f^2(r) r^2 \mathrm{d}r - \frac{16}{9}\pi^2 a_0^3 (sr_0)^3\,. \end{aligned} \tag{21}$$

In equation (20) and (21) and in the following we are using atomic units: distances are expressed in Bohr radii a_0, potential in e/a_0, electron density in $1/a_0^3$, and the wave vector in $1/a_0$ units.

Equation (21) can be further transformed. We make use of the relationship between the Fermi wave number and the electrostatic potential

$$k_f^2/2 = V(r)$$

where

$$V(r) = \frac{Z}{r} - \frac{1}{r}\int_0^r D(t)\mathrm{d}t - \int_r^{\infty} \frac{D(t)}{t}\mathrm{d}t$$

and Z is the charge of the nucleus.

This relationship together with equation (14) leads to the final form of the incoherent scattering function in Fermi-gas approximation.

$$\begin{aligned} I_i(s)/I_{\mathrm{cl}} = \int_{r_0(s)}^{\infty} D(r)\mathrm{d}r + 8a_0 s\int_0^{r_0(s)} V(r) r^2 \mathrm{d}r \\ - \frac{16}{9}\pi^2 a_0^3 (sr_0)^3, \end{aligned} \tag{22}$$

$r_0(s)$ is determined from the equation

$$\left(\frac{6\pi D(r_0)}{r_0^2}\right)^{1/3} - 4\pi a_0 s = 0\,, \tag{23}$$

where $D(r)$ is the radial electron density.

Equation (22) also contains the contribution of the exchange effect. This is evident, considering that (22) was obtained by approximation on the basis of equation (8).

The first term of the expression gives the number of electrons outside the sphere of radius r_0. Thus this term is sensitive to the behaviour of the radial electron density in the outer part of the r range, while the second term is sensitive to the potential function within r_0. The function $r_0(s)$ can be qualitatively examined by substituting the electronic density of the hydrogen 1s state into (23),

$$\exp\left(-\tfrac{2}{3}r_0\right) \sim s \, .$$

We can see that there is a certain reciprocity relation between the scattering variable s and r_0.

It is to be noted that the philosophy of Heisenberg's approximation for the incoherent scattering functions of the atoms on the basis of the TF atomic model is similar to that of the above treatment. However our equation (22) is more generally valid because it does not restrict itself to the TF atomic model. The given expression for the incoherent intensities in the Fermi-gas approximation represents the dependence of the incoherent scattering functions of an N-electron system (atom or ion) on its radial electron density and its electrostatic potential. The statement implied in (22) is of the same character as that stating the coherent scattering function to be the square of the Fourier transform of the radial electron density. There is a difference between the two statements in their validity ranges: the latter is generally valid including Fermi-gas approximation (as shown above) whereas statement (22) is valid only for this approximation.

3. Numerical results

Equation (22) will be applied below for the TF and TFD models. We use in these models potential and electron density functions derived from approximate analytical screening factors of the same form. Screening factors of the form

$$Z_p(r)/Z = \sum_i^m \gamma_i \exp\{-\lambda_i r\} \qquad (24)$$

have been determined for the TF atomic model by Rosenthal (1936) and for the TFD model by Bonham & Strand (1963).

The radial electron density and the complete electrostatic potential corresponding to (24) are the following

$$D(r) = Zr \sum_{i=1}^{m} \gamma_i \lambda_i^2 \exp\{-\lambda_i r\}$$

and

$$V(r) = \frac{Z}{r}\,\frac{Z_p(r)}{Z} \, .$$

With these expressions equation (22) and (23), needed for the determination of the incoherent scattering function, become analytical.

With the introduction of the notation

$$x_i = \lambda_i r_0(s)$$

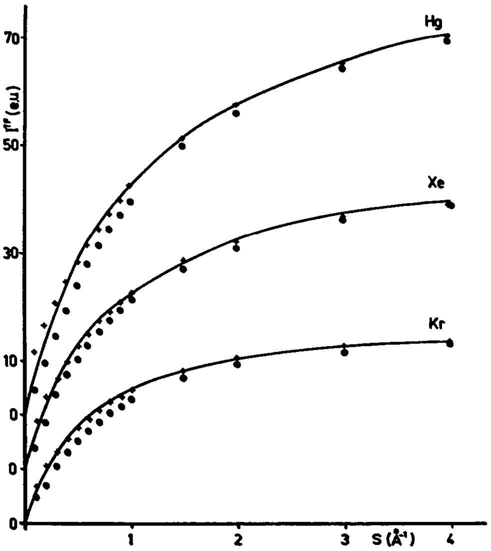

Fig. 2. Incoherent intensity functions I^{TF} calculated from the TF model (−) compared to values I^{HB} of Heisenberg–Bewilogua (+) and I^{CR} of Cromer (●).

Table 1. *Exchange energy values* (a.u.) *determined by the sum-rule procedure and calculated from different atomic models*

Z	$TF_{s.r.}$	TF_{cal}	$TFD^*_{s.r.}$	TFD_{cal}	HF $SCF_{s.r.}$
Ar 18	26·28	26·31	31·03	28·16	29·46
Fe 26	48·86	48·53	55·10	51·31	
Ga 31	65·73	65·03	72·58	68·39	
Kr 36	84·54	83·41	91·70	87·30	90·57
Rb 37	88·52	87·92	95·72	91·29	
Cd 48	136·59	134·60	143·56	139·50	
Xe 54	165·90	163·70	172·36	169·10	171·02
La 57	181·28	179·10	187·42	184·60	
Gd 64	219·03	217·10	224·28	223·10	
Yb 70	253·25	252·00	257·67	258·20	
Hg 80	313·85	314·60	316·97	321·50	315·61
U 92	391·84	396·80	394·07	404·80	

(22) and (23) obtain the following form

$$I_i(s)/I_{\mathrm{cl}}=Z\sum_i^m \gamma_i(x_i+1)\exp\{-x_i\}+8a_0sZ\sum_i^m \frac{\gamma_i}{\lambda_i^2}\times[1-(x_i+1)\exp\{-x_i\}]-\frac{16}{9}\pi^2a_0(sr_0)^3 \quad (25)$$

and

$$\left[\frac{6\pi Z\sum_i^m \gamma_i\lambda_i^2\exp\{-x_i\}}{r_0}\right]^{1/3}-4\pi a_0s=0. \quad (26)$$

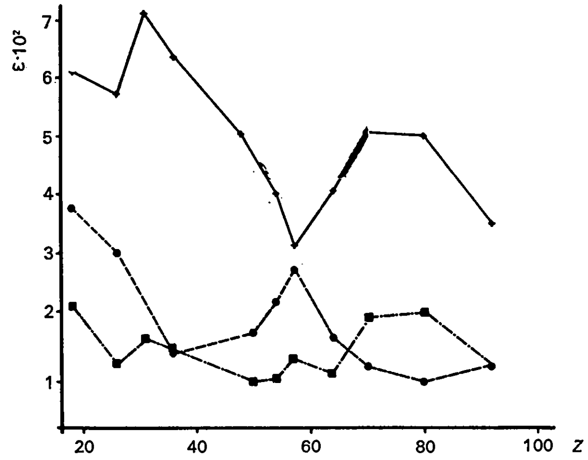

Fig. 3. Standard deviations of the present intensities from I^{CR} for several atoms and calculated from TFD* (■), TFD (●), TF (+) models.

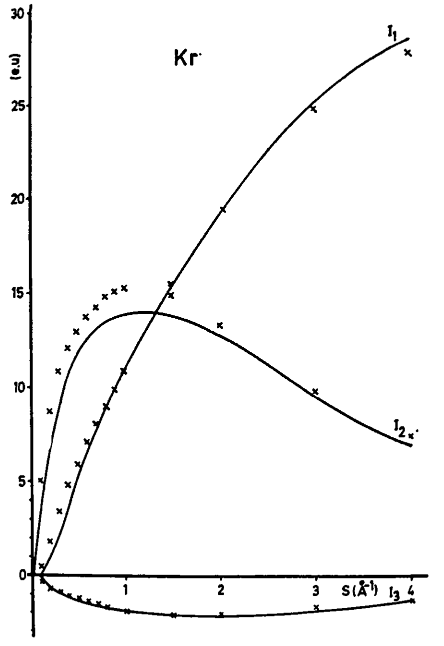

Fig. 4. Plot of the three terms of equation (22) *vs.* s in the example of the Kr atom. Comparison of TFD* (−) and TF (×) data.

γ_i and λ_i are atomic parameters. The dimensions of λ_i are $1/a_0$. With the use of (25) and (26), and on the basis of the TF and TFD atomic models, incoherent scattering functions have been computed for a series of atoms covering the atomic number range from $Z=18$ to 92 (notation below I^{model}).

The accuracy of these calculations was checked in two ways: firstly by comparing the results with those of Cromer (1967, 1969) who used the WH theory and HF atomic model (Cromer's values are denoted by I^{CR}), and secondly by a sum-rule procedure. In this comparison

$$\varepsilon^{\mathrm{model}}=\frac{1}{Z}\sqrt{\frac{\sum\delta_i^2}{n-1}}, \quad \text{with} \quad \delta_i=I^{\mathrm{model}}(s_i)-I^{\mathrm{CR}}(s_i),$$

was taken as the measure of deviation.

Here n is the number of scattering variable values at which comparisons were made. Since in experimental X-ray work $s<1{\cdot}2$, ε was somewhat weighted in favour of this range by choosing the following 15 s-values for the comparison 0, 0·1, 0·2, ... 1·0, 1·5, 2, 3, 4.

Another estimation of the accuracy was made by examining the so-called sum rule (Tavard, 1966). The two-particle contribution to the potential energy of the scattering atom is

$$\int_0^\infty [I_i(s)/I_{\mathrm{cl}}-N]\mathrm{d}s=\pi\left\langle\frac{1}{r_{12}}\right\rangle=\tfrac{1}{2}\sum_i\sum_{j\neq i}V_{ij}. \quad (27)$$

Between the exchange-energy term (together with the self-exchange energy) of the two-particle potential energy and the incoherent scattering function there exists the following relationship:

$$-\mathscr{I}_{\mathrm{exch}}=\int_0^\infty [N-I_i(s)/I_{\mathrm{cl}}]\mathrm{d}s=\pi\left\langle\frac{1}{r_{12}}\right\rangle_{\mathrm{exch}}. \quad (28)$$

On the other hand, the values of $\mathscr{I}_{\mathrm{exch}}$ can be determined in a statistical way according to

$$-\mathscr{I}_{\mathrm{exch}}=\tfrac{1}{2}\int V_{\mathrm{exch}}\varrho\,\mathrm{d}V \quad (29)$$

where

$$V_{\mathrm{exch}}=\tfrac{3}{2}\left(\frac{3}{\pi}\right)^{1/3}\varrho^{1/3}$$

is the Slater exchange potential.

In our calculations the exchange energies were determined in both ways for the different atomic models.

$\mathscr{I}_{\mathrm{cal}}^{\mathrm{model}}$ denotes the values obtained from (29) and $\mathscr{I}_{s.r}^{\mathrm{model}}$ those calculated from (28) with scattering functions from (25) and (26).

Integrations were performed numerically in both (28) and (29) by use of the standard Simpson method. For this purpose the integrands in (28) had been determined in the range $0\leq s\leq 14$. For the sake of comparison, in some cases $\mathscr{I}_{s.r}^{\mathrm{CR}}$ from the incoherent scattering functions of Cromer were also determined the functions having been extrapolated in the range $8\leq s\leq 14$.

3.1 *Incoherent scattering of TF atoms*

For the TF model equation (24) was used with parameters given by Rosenthal. With the help of (25) and (26) the incoherent scattering functions were determined for a number of elements. As illustrative examples those of Kr, Xe and Hg are shown in Fig. 2. The same Figure contains the corresponding I^{CR} functions, and the values of the Heisenberg–Bewilogua function I^{HB} as well (Pálinkás, 1973). It can be seen that our functions agree well with those obtained from the HB function. This is evident, because – as can easily be shown – in the case of the TF model Heisenberg's equation is equivalent to equation (22). It is known that the TF model takes no account of the exchange effect, but, as mentioned in § 2.2, equation (24) was derived with allowance for the exchange. For this reason the contribution of this effect will be present in the incoherent scattering function. From Table 1 it can be seen that the exchange energy values obtained by the sum rule ($\mathscr{I}^{\mathrm{TF}}_{s.r}$) and those calculated from TF electron densities ($\mathscr{I}^{\mathrm{TF}}_{\mathrm{cal}}$) agree well for all the atomic numbers. They are, however, lower than the corresponding values from TFD and HF SCF atomic models (Table 1).

The relatively high values of $\varepsilon^{\mathrm{TF}}$ (Fig. 3) compared to those of the other models can be explained by the fact that the TF electrostatic potential and the radial electron density over the outer range are both higher than those of the other models. (The TF atom is more expanded.) The higher contribution of these functions to the scattered intensities (one of them for small s values, the other over nearly the whole s range) is illustrated also in the case the Kr atom in Fig. 4. These contributions are further increased because the integration limit r_0 grows more rapidly with decreasing s as a second consequence of the higher $D(r)$, (Fig. 5).

3.2 *Incoherent X-ray scattering of the TFD atoms*

For the TFD model, analytic screening factors were used with the atomic parameters given by Bonham & Strand. Fig. 3 shows that the $\varepsilon^{\mathrm{TFD}}$ values pertaining to the incoherent intensities derived from the TFD densities and an electrostatic potential are smaller than those from the TF model, *i.e.* they approximate more closely the scattering functions calcultaed from the HF WH theory. Table 1 also shows that the $\mathscr{I}^{\mathrm{TF}}_{s.r}$ exchange energies are somewhat larger than the $\mathscr{I}^{\mathrm{CR}}_{s.r}$ values for all atomic numbers.

A further improvement of the TFD results could be achieved by modifying the only physical constant in equation (22), the Bohr radius a_0. Gáspár (1969) has pointed out that starting from an atomic model constructed of hydrogen-like one-electron orbitals, a TF-like model could be obtained in zero-order approximation of E/Z^2. According to this theory, the electron shell of the atom is a free-electron gas where the electrons – quasiparticles – possess a reduced mass of $m = 0{\cdot}9273 m_e$.

Using this result in the theory of § 2.2, a_0 in equation (22) and (23) changes to $a^* = 1{\cdot}0785\ a_0$. In the Figures and in the text below the incoherent scattering values and other derived quantities computed from the modified equations (22) and (23) are indexed by an asterisk (*). This modification has resulted in further reduction of the $\varepsilon^{\mathrm{TFD*}}$ values, (Fig. 3). $I^{\mathrm{TFD*}}$ scattering functions have been also computed for a series of elements covering the periodic system (Fig. 6). In this Figure the corresponding I^{CR} values are also shown. Evidently, our results agree very well with those of the more correct WH theory. Similary, a good coincidence of $\mathscr{I}^{\mathrm{TFD*}}_{s.r}$ and the $\mathscr{I}^{\mathrm{CR}}_{s.r}$ exchange energies was also found, (Table 1). It can also be seen from Table 1 that the exchange energies calculated by the sum rule agree with good accuracy with the $\mathscr{I}^{\mathrm{TFD}}_{\mathrm{cal}}$ values calculated from the model. Remaining small deviations of the incoherent scattering functions $I^{\mathrm{TFD*}}$ from those calculated with WH theory originate partly from the approximating character of equation (22) and (23), partly from the deficiencies of the model, the errors of the analytic fits included. The dependence of the terms in the modified equation (22) on the scattering variable is shown in Fig. 4 for the example of the Kr atom. The relationship between r_0 and s, also for the Kr atom, is illustrated in Fig. 5. The 'reciprocity' between the variables is evident.

4. Discussion of the results

Our results can be summarized as follows: (i). A relationship has been found between the incoherent scattering function on one part, and the electrostatic potential and the radial electron density of an N-electron system on the other [equations (22) and (23)]. This relationship can be interpreted in terms of a physical picture: for small values of the scattering variable (X-ray scattering range: $s < 1{\cdot}2$) the major contribution to the incoherent

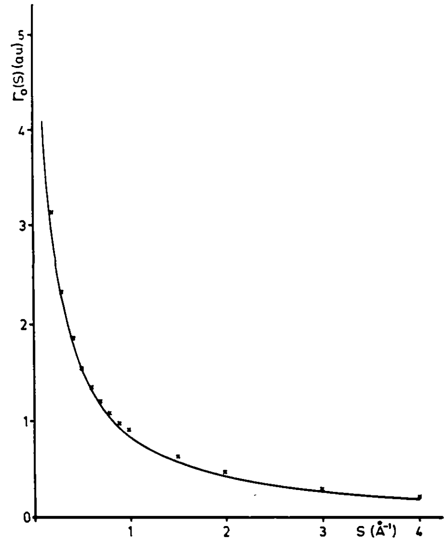

Fig. 5. Plot of r_0 *vs.* s as calculated from TFD* (–) and TF (×) models of the Kr atom.

scattering function is furnished by the electrostatic potential. A small quantity of electric charge, that of the outer electrons, makes a classical contribution to the scattering. Since the electrostatic potential is sensitive to various correlation effects over nearly the entire range and, moreover, the electron density is influenced by these effects in the outer r range (Fig. 4), it is comprehensible that the incoherent scattering is modified by them in the region of small s values (Bartell & Gavin, 1964). At high values of s (large momentum transfer) the dominant contribution is furnished by the electron density. The atom behaves more and more like a classical N-charge. When atom the is treated as a classical N-charge ($r_0=0$) equation (22) becomes

$$I_i(s)=N\,.\,I_{\rm cl}\,.$$

This is the Thompson cross section.

(ii) Atomic incoherent scattering functions have been determined on the basis of the TFD statistical atomic model. They represent a better approximation to those derived from WH theory on the basis of the HF model than does the Heisenberg–Bewilogua function.

A test of the HF SCF model, the determination of the incoherent scattering functions of heavy ions and the examination of the influence of correlation effects will be treated in following papers.

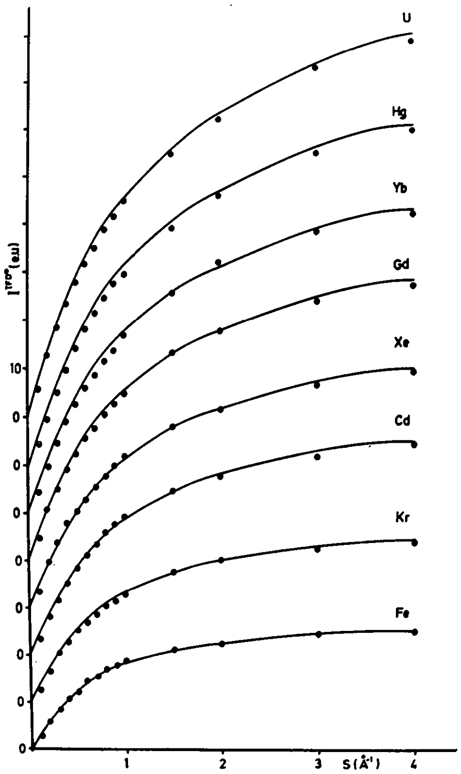

Fig. 6. Incoherent intensity functions $I^{\rm TFD*}$ calculated from the TFD model by the use of modified equations (22) and (23) compared to $I^{\rm CR}$ values of Cromer (●).

Computation of the atomic incoherent intensities at 15 s values with the aid of equation (25) and (26) took less than 20 s on a CDC 3300 computer, irrespective of the atomic number.

Note added in proof: Two important contributions to the subject of this paper escaped the author's attention, both in *Phys. Rev.* A 5, No 2 (1971). L. B. Mendelson & F. Biggs (pp. 688–691) have extended Heisenberg's derivation to include the TFD model. D. E. Parks & M. Rotenberg (pp. 551–526), applying the theory of the homogeneous interacting electron gas and the TFD atomic model have derived the incoherent scattering as a function of the electron density. This is similar equation to our equation (22), which is a function of the electron density and the electrostatic potential.

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