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## Relativistic Corrections to the Kinematic X-ray Scattering in the Pauli Approximation

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### Abstract

Expressions for the kinematic scattering of X-rays by electrons are obtained from the Pauli Hamiltonian. In addition to the modified electron density, relativity is shown to contribute with an additional term, the kinetic form factor. A formula for this term is given for one-electron atoms.

### 1. Introduction

Relativistic quantum mechanics leads in some cases to a considerable modification of the electron distribution in atoms, molecules and solids as compared to non-relativistic results, and the use of relativistic electron densities in the calculation of atomic form factors for X-ray crystallography has become standard (Cromer & Waber, 1974; see also Hubbell & Øverbø, 1979). In the present paper, we study the impact of relativistic theory on the equations for the scattering amplitude. Our study is based on the Pauli equation, which represents the conceptually simplest

approach, where comparison with the non-relativistic expressions is most straightforward. In addition, this approach has the advantage of being independent of the choice of relativistic  $N$ -particle theory, which is still a problem containing many unsettled questions (Grelland, 1981; Mittleman, 1981; Sucher, 1980; Buchmüller & Dietz, 1980). All theoretical approaches to this problem lead to the Pauli equation in the first approximation. The calculation results presented in § 4 show that the Pauli approximation is adequate for the present purpose. With this method it becomes possible to relate the relativistic corrections due to relativistic scattering theory directly to the form of the non-relativistic wave function. Thus a transparent picture of the form and size of the correction is provided, which can be used in relativistic electron density studies based on X-ray crystallographic measurements.

The present theory is restricted to the first Born approximation, and higher-order effects (anomalous scattering) must be added by a separate calculation. Thus, the method cannot be directly compared to

methods based on second-order theory in the Dirac representation (see, however, the comment in § 4 on the results of Cromer & Liberman, 1970). Note that the unitary transformation relating the two representations does not conserve the order-by-order expansion in  $c^{-2}$ . [A derivation of the first Born scattering expression in the Dirac representation is given by Grelland (1984).]

The non-relativistic theory of purely elastic kinematic (*i.e.* first Born approximation) scattering is reviewed by *e.g.* Feil (1977), where further details can be found (note the different choice of electromagnetic units). In this theory, the scattering factor  $F(\mathbf{q})$  is a functional of the electron density  $\rho(\mathbf{x})$ ,

$$F(\mathbf{q}) = \int_{\mathbb{R}^3} \rho(\mathbf{x}) \exp(-i\mathbf{q} \cdot \mathbf{x}) \, d\mathbf{x}, \quad (1)$$

where

$$\rho(\mathbf{x}) = \sum_{\text{all spin}} \int_{\mathbb{R}^{3N-3}} |\psi(\mathbf{x}\mathbf{x}_2 \dots \mathbf{x}_N)|^2 \, d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (2)$$

and  $q = |\mathbf{q}| = 4\pi \sin(\frac{1}{2}\theta)/\lambda$ ,  $\lambda = \text{X-ray wavelength}$ ,  $\theta = \text{scattering angle}$ ,  $N = \text{number of electrons}$ . In the Hartree-Fock approximation, which is the one usually applied for the calculation of  $\rho$ ,

$$\rho(\mathbf{x}) = \sum_j |\varphi_j(\mathbf{x})|^2, \quad (3)$$

where  $\{\varphi_j\}$  are the orbitals. We will reserve the word form factor to mean the function  $F(\mathbf{q})$  defined by (1). We will show that the relativistic scattering factor within the  $1/c^2$  approximation is the form factor with the relativistic density plus the more complicated term (14), depending on  $\varphi^2\varphi$ , which we denote the kinetic form factor.

We will restrict ourselves to the treatment of atomic (kinetic) form factors, since this is the only place in the theory where the relativistic corrections are of any importance for X-ray crystallography. As is customary, we assume spherical symmetry, which implies that (1) can be replaced by

$$F(q) = (1/q) \int_0^\infty \rho(r) \sin(qr) r \, dr. \quad (4)$$

Moreover, spin-dependent photon-electron coupling terms will be neglected.

## 2. The Pauli approximation

Before considering the relativistic scattering factor, we make some remarks on the nature of the Pauli approximation.

The Pauli equation is a perturbation equation. This means that it cannot be solved as an eigenvalue equation  $H_p\psi = E\psi$ , where

$$H_p = H_s + V \quad (5)$$

$$V = - \sum_{j=1}^N [p_j + (e/c)\mathbf{A}_j]^4 / 8m^3c^2 + H_{\text{spin}} + H_{\text{Darwin}} \quad (6)$$

and  $H_s$  is the Schrödinger Hamiltonian (Moss, 1973, p. 176). In fact,  $H_p$  has quite surprising properties (Almlöf, Faegri & Grelland, 1984). It has no lower bound to the energy, and it has no bound eigenstates. Mathematically,  $H_p$  has a continuous spectrum that is unbounded below (but bounded above!). However, the Pauli Hamiltonian represents a proper relativistic approximation if  $V$  is used as a perturbation on the eigensolutions of  $H_s$ .

Let  $\rho_R = \rho_0 + \Delta\rho$  be the relativistically corrected electron density, where  $\rho_0$  is the non-relativistic one. Then  $\Delta\rho$  may be calculated from the wave function  $\psi$ , which may be obtained in one of two ways.

The lowest-order correction to  $\psi$  can be calculated by perturbation theory, with  $V$  as the perturbation. Or else, the relativistically corrected  $\psi$  can be obtained from a Dirac-type wave function by a Pryce-Foldy-Wouthuysen transformation, see *e.g.* Snijders & Pyykkö (1980). This procedure is sufficiently accurate in a  $c^{-2}$  approximation. Note that the Dirac densities cannot be used directly, because they belong to a different representation. Physically, they are probability distributions over a different kind of position.

We also note that the order-by-order argument of perturbation theory implies that the kinetic form factor can be calculated from a non-relativistic wave function to give a  $c^2$  accuracy.

## 3. The kinetic form factor

Kinematic scattering is induced by interactions quadratic in the components of the photon field. From the non-relativistic kinetic energy

$$T = [\mathbf{p} + (e/c)\mathbf{A}]^2 / 2m \quad (7)$$

we obtain the quadratic term

$$U_0 = (e^2/2mc^2)\mathbf{A}^2, \quad (8)$$

where  $-e = \text{electron charge}$ ,  $m = \text{electron mass}$  and  $\mathbf{A}$  is the Coulomb gauge photon field. This term leads to a scattering factor of the form (1) (Feil, 1977).

From the first-order relativistic correction to the kinetic-energy expression

$$T_1 = -[\mathbf{p} + (e/c)\mathbf{A}]^4 / 2m(2mc)^2, \quad (9)$$

we obtain two quadratic terms

$$U'_1 = -[e^2/2mc^2(2mc)^2](\mathbf{A}^2\mathbf{p}^2 + \mathbf{p}^2\mathbf{A}^2) \quad (10)$$

$$U''_1 = -[4e^2/2mc^2(2mc)^2](\mathbf{A} \cdot \mathbf{p})^2. \quad (11)$$

It is shown by a straightforward integration over the angular components in the spherical coordinate system that

$$3\langle(\mathbf{A} \cdot \mathbf{p})^2\rangle = \langle\mathbf{A}^2\mathbf{p}^2\rangle = \langle\mathbf{p}^2\mathbf{A}^2\rangle \quad (12)$$

for a spherically symmetric electronic state. Hence,

$U'_1 + U''_1$  may be replaced by the operator equivalent

$$U_1 = -\frac{5}{6}(1/m^2c^2)U_0p^2, \quad (13)$$

from which one derives, in analogy with the non-relativistic treatment, the kinetic form factor

$$K(q) = -(5/6m^2c^2)q^{-1} \int_0^\infty \eta(r) \sin(qr)r \, dr. \quad (14)$$

In the one-particle case (or for the orbital contribution in the Hartree-Fock case),  $\eta$  has the form

$$\eta(r) = -\bar{\psi}(r)r^{-2}d[(r^2d/dr)\psi(r)]/dr. \quad (15)$$

In the  $N$ -particle case:

$$\eta(r) = -Nr^{-2}dr[(r^2d/dr)\rho(r;r')]/dr|_{r=r'}, \quad (16)$$

where  $\rho(r;r')$  is the non-diagonal first-order density matrix (McWeeny & Sutcliffe, 1969, ch. 4).

The total scattering factor becomes

$$F_{\text{tot}}(q) = F(q) + \Delta F(q) + K(q), \quad (17)$$

where

$$\Delta F(q) = (1/q) \int_0^\infty \Delta\rho(r) \sin(qr)r \, dr. \quad (18)$$

In this paper, we have mainly considered the term  $K(q)$ . To obtain the total relativistic correction to  $S(q)$ ,  $\Delta F(q)$  has to be calculated as well. This is the object of a forthcoming paper (Grelland, 1985).

To give an idea of the behaviour of the kinetic form factor, we have derived the formula for a hydrogen-like atom with nuclear charge  $Z$  in the ground state, *i.e.* with the wave function

$$\psi(r) = 2Z^{3/2} \exp(-Zr). \quad (19)$$

The non-relativistic form factor is given by the formula

$$F(x) = Z^4(Z^2 + 4\pi^2a_0^2x^2)^{-2}, \quad (20)$$

where  $x = \sin(\theta/2)/\lambda$  ( $\text{\AA}^{-1}$ ) =  $q/4\pi a_0$ , and  $a_0$  is the Bohr radius in ångströms. Equations (14), (15) and (19) combine to give the correction formula

$$K(x) = \frac{5}{6}\alpha^2 Z^6(Z^2 + 4\pi^2a_0^2x^2)^{-2} - \frac{5}{3}\alpha^2 Z^5(Z^2 + 4\pi^2a_0^2x^2)^{-1}, \quad (21)$$

where  $\alpha$  is the fine-structure constant.

#### 4. Comments

The kinetic form factor can be seen from (21) to be small, but within the accuracy of the standard tables of form factors used in crystallography. Its size for  $x=0$  is closely related to the binding energy of the electron. From the virial theorem, we have at  $x=0$ :

$$\begin{aligned} K(0) &= -5\langle p^2 \rangle / 6m^2c^2 \\ &= -5\langle T \rangle / 3mc^2 \\ &= 5E / 3mc^2. \end{aligned} \quad (22)$$

It is interesting to note that (22) equals expression (19) of Cromer & Liberman (1970). This indicates that the term  $-f_0^+ + f^- - f_0^-$  of that paper corresponds to the correction that we identify as due to relativistic interaction, while  $f^+$  represents the proper anomalous scattering in the usual sense. Such a conclusion is valid only close to the non-relativistic limit.

The presence of the kinetic form factor puts a limit on the accuracy in the direct determination of electron densities from scattering factors through (1), in particular in the relativistic domain. To increase the accuracy, one will probably have to go *via* a determination of the non-diagonal first-order density matrix (16) and a calculation of the function

$$\rho(r) - 5\eta(r)/6m^2c^2, \quad (23)$$

which is the inverse Fourier transform of the total scattering factor. The function  $\eta(r)$  is known to be very sensitive to the form of the wave function (Grelland & Almlöf, 1982).

The present method represents a substantial simplification, both conceptual and calculational, compared to the traditional methods using the Dirac representation. Since the correction can be calculated from non-relativistic wave functions, it is possible to use wave functions of high accuracy, *e.g.* including correlation. Moreover, the result is easy to compare to the non-relativistic approximation, since the same representation is used, and since the total scattering factor has the form of a sum of various physical interpretable terms, (17).

I am indebted to one of the referees for drawing my attention to the result of Cromer & Liberman mentioned in § 4.

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