

Coherent X-ray Scattering by Co III

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Abstract

The atomic scattering factor for the ground state of the cobalt ion, $3d^7 4F$, has been evaluated using nonrelativistic and 'relativistic-corrected' wavefunctions of varying accuracy. The importance of incorporating all types of electron correlation systematically within the valence subshell while keeping a fixed argon core is discussed. From the results presented, it appears that atomic scattering factors evaluated using Hartree-Fock wavefunctions are of sufficient accuracy for an atomic ion with an open-shell ground-state configuration.

1. Introduction

Early attempts to calculate atomic scattering factors were made by Freeman (1959) and Freeman and Wood (1959) using available Hartree and Hartree-Fock atomic wavefunctions. Hanson *et al.* (1964) carried out a more extensive calculation using the Herman-Skillman self-consistent field wavefunctions. Cromer and Waber (1965) incorporated relativistic effects by using Dirac-Slater atomic wavefunctions, while relativistic Hartree-Fock atomic scattering factors were calculated by Doyle and Turner (1968) using the relativistic Hartree-Fock wavefunctions of Coulthard (1967). A compilation of these and other results has been given in the 'International Tables for X-ray Crystallography' (Cromer and Waber 1974).

The role that atomic scattering factors play in crystallographic studies for the determination of crystal structure problems is well known (Bonham and Fink 1974). Accurate knowledge of the atomic scattering factor is also necessary in X-ray diffraction measurements on amorphous solid or liquid samples in order to obtain information regarding the radial distribution functions of the particles (Norten and Levy 1971; Lie and Clementi 1975).

The limitations of the Hartree-Fock approximation for the evaluation of atomic scattering factors have been investigated by Bartell and Garvin (1964, 1965), Kohl and Bonham (1967), Kim and Inokuti (1968) for helium and by Brown (1970*a*) for the helium isoelectronic sequence. The neglect of electron-correlation effects has also been considered by Brown (1970*b*) for the lithium and beryllium isoelectronic sequence and by Brown (1971) for neutral carbon. It was shown that the error in the atomic scattering factor due to the neglect of the electron correlation is approximately 1% for elements with $Z \leq 6$.

The present investigation extends the study of correlation effects for evaluating atomic scattering factors to an atomic ion with an open-shell ground-state configuration. For heavier atoms, relativistic effects become important and atomic scattering factors determined using nonrelativistic wavefunctions could be inaccurate. According to Øverbø (1977), for heavier atoms with $Z \geq 20$, relativistic effects become important and atomic scattering factors based on any nonrelativistic wavefunctions are inaccurate at small momentum transfer. It is also our aim here to consider the consequences of including relativistic effects.

2. Theory

For an N -electron atomic system the atomic form factor or atomic scattering factor is defined as

$$F(q) = \langle \psi(LS) | \sum_{j=1}^N \exp(i \mathbf{q} \cdot \mathbf{r}_j) | \psi'(L'S') \rangle, \quad (1)$$

where $\psi(LS)$ is the ground-state wavefunction, \mathbf{q} is the momentum transfer vector with magnitude

$$q = |\mathbf{q}| = (4\pi/\lambda) \sin \frac{1}{2}\theta, \quad (2)$$

θ is the angle between the directions of the incident and scattered photons, λ is the wavelength of the incident photon, \mathbf{r}_j is the position vector of the j th electron and the summation is over all the electrons. In X-ray scattering, the variable $(\sin \frac{1}{2}\theta)/\lambda = q/4\pi$ is commonly used in place of q .

If the coordinate system is chosen so that the momentum change is in the z direction of position, the operator in equation (1) may be written as

$$\exp(i \mathbf{q} \cdot \mathbf{r}_j) = \sum_k i^k (2k+1) C_0^{(k)}(\hat{\mathbf{r}}_j) j_k(qr_j), \quad (3)$$

where $j_k(qr_j)$ is a spherical Bessel function and the components of the tensor $\mathbf{C}^{(k)}$ satisfy the equation

$$C_v^{(k)} = \left(\frac{4\pi}{2k+1} \right)^{1/2} Y_k^v. \quad (4)$$

The function $F(q)$ plays an important role in the theory of scattering of X rays and electrons by atoms. When the energy of an incident photon is much smaller than the rest energy mc^2 of an electron, the differential cross section $d\sigma_c$ for coherent scattering of the photon by the atom into the solid-angle element $d\Omega$ is

$$d\sigma_c = \frac{1}{2} r_0^2 (1 + \cos^2 \theta) |F(q)|^2 d\Omega, \quad (5)$$

where $r_0 = e^2/mc^2$ is the classical electron radius and $\frac{1}{2} r_0^2 (1 + \cos^2 \theta)$ is the Thomson cross section for scattering by a free electron. In equation (5), $|F(q)|^2$ may be interpreted as the effective number of electrons contributing to the coherent scattering.

Coherent scattering of X rays corresponds to elastic scattering of fast electrons. The differential cross section $d\sigma_e$ for elastic scattering of electrons by an atom, in the first Born approximation, is

$$d\sigma_e = \frac{4a_0^2}{(Ka_0)^4} |Z - F(q)|^2 d\Omega, \quad (6)$$

where $a_0 = \hbar^2/mc^2$ is the Bohr radius. In this case we may interpret $F(q)$ as representing the effective shielding of the nuclear charge Z .

3. Radial Functions

The radial functions used in the calculations were determined in an LS coupled representation of the atomic states. The atomic state wavefunctions are represented by the configuration interaction expansion

$$\Psi(LS) = \sum_{i=1}^M c_i \Phi_i(\alpha_i; LS), \quad (7)$$

where L and S are the total orbital and spin angular momentum, $\{\alpha_i\}$ defines the angular momentum coupling scheme of the i th configuration, and M is the total number of configurational functions $\{\Phi_i\}$ constructed from the one-electron functions (spin orbitals)

$$u(r, m_s) = r^{-1} P_{nl}(r) Y_l^{m_l}(\theta, \phi) \chi(m_s). \quad (8)$$

The radial functions $P_{nl}(r)$ are expanded in analytic form as

$$P_{nl}(r) = \sum_{j=1}^k C_{jnl} r^{jnl} \exp(-\zeta_{jnl} r), \quad (9)$$

where $k \geq n-l$. We also require the radial functions, for a given value of l , to form an orthonormal set:

$$\int_0^\infty P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'}; \quad l+1 \leq n' \leq n. \quad (10)$$

The 1s, 2s, 2p, 3s, 3p and 3d functions were taken as the Hartree-Fock functions of the $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ 4F state (Clementi and Roetti 1974). Correlation functions were determined to describe the important $3d^2 \rightarrow l^2$ correlation effect as follows: The 4p and 4d correlation functions were optimized on the lowest 4F state obtained from the configurational functions

$$3d^7, \quad 3d^5(^4F)4p^2(^1S), \quad 3d^5(^4F)4p^2(^1D), \quad 3d^5(^4G)4p^2(^1D);$$

$$3d^7, \quad 3d^5(^4F)4d^2(^1G), \quad 3d^5(^4G)4d^2(^1G), \quad 3d^5(^4G)4d^2(^3F)$$

respectively. The 4s and 4f correlation functions were determined respectively by optimizing on the lowest 4F state of the two configurational functions

$$3d^7, \quad 3d^5(^4F)4s^2$$

and the three configurational functions

$$3d^7, \quad 3d^5(^4F)4f^2(^1S), \quad 3d^5(^4F)4f^2(^3P).$$

Table 1. Correlation orbital exponents for Co III

nl	I_{jnl}	ζ_{jnl}	nl	I_{jnl}	ζ_{jnl}	nl	I_{jnl}	ζ_{jnl}
4s	1	20.90200	4p	2	10.98930	4d	3	6.14557
	2	8.25433		3	4.96208		4	2.55863
	3	5.78433		4	3.32219			
	4	3.06067				4f	4	4.51943

In obtaining the correlation functions we have chosen

$$k = n - l,$$

so that the coefficients $\{C_{jnl}\}$ are determined uniquely by equation (10). We also choose

$$I_{jnl} = l + j, \quad j \geq 1$$

in (9) so that the freely varying parameters are the exponents $\{\zeta_{jnl}\}$. The correlation orbital exponents are given in Table 1.

Table 2. Nonrelativistic atomic scattering factor $F(q)$ for Co III (see Section 4)

$(\sin \frac{1}{2}\theta)/\lambda$ (\AA^{-1})	A	B	C	D
0.00	25.0000	25.0000	25.0000	25.0000
0.05	24.7174	24.7217	24.7195	24.7196
0.10	23.9089	23.9246	23.9166	23.9170
0.15	22.6786	22.7095	22.6941	22.6947
0.20	21.1643	21.2102	21.1878	21.1887
0.25	19.5044	19.5620	19.5349	19.5358
0.30	17.8162	17.8805	17.8515	17.8523
0.40	14.6725	14.7361	14.7104	14.7107
0.50	12.0996	12.1507	12.1328	12.1325
0.60	10.1591	10.1947	10.1842	10.1837
0.70	8.7665	8.7885	8.7834	8.7829
0.80	7.7901	7.8018	7.8000	7.7996
0.90	7.1007	7.1054	7.1055	7.1052
1.10	6.1910	6.1891	6.1903	6.1902
1.30	5.5265	5.5231	5.5242	5.5243
1.50	4.9197	4.9175	4.9175	4.9176
1.70	4.3383	4.3362	4.3367	4.3368
1.90	3.7983	3.7969	3.7972	3.7973
2.10	3.3180	3.3172	3.3173	3.3174

4. Results and Discussion

Using the Hartree-Fock radial functions of Clementi and Roetti (1974) for the $3d^7$ 4F state of Co III the nonrelativistic Hartree-Fock atomic scattering factor was evaluated. The results are presented in entry A of Table 2. Using the correlation

functions determined in Section 3 nonrelativistic atomic scattering factors were evaluated using configuration interaction wavefunctions of various accuracy. The atomic scattering factor is given in terms of one-electron operators so it is natural that the one-electron excitation should have a significant effect. Since we are investigating the effect of including correlation effects within the valence subshell, while keeping a fixed argon core, it follows that the most important single electron excitation will be the $3d \rightarrow nd$ excitation. A nonrelativistic wavefunction was determined by including the configurations

$$3d^7, \quad 3d^64d \quad (11)$$

in expansion (7). The results are presented in entry B of Table 2. It is seen that the atomic scattering factor is larger at small momentum transfer but marginally smaller at the higher momentum transfer $[(\sin \frac{1}{2}\theta)/\lambda > 0.90 \text{ \AA}^{-1}]$.

The next stage of our investigation was the inclusion of the two-electron excitations $3d^2 \rightarrow l^2$. It follows that the most important pair electron excitation will be $3d^2 \rightarrow nd^2$. A nonrelativistic wavefunction was determined by including the configurations

$$3d^7, \quad 3d^64d, \quad 3d^54d^2 \quad (12)$$

in expansion (7) and forming all possible configurational functions. The results are presented in entry C of Table 2. It is seen that the inclusion of $3d^2 \rightarrow nd^2$ pair correlation excitations results in a reduction of the atomic scattering factor at small momentum transfer $[(\sin \frac{1}{2}\theta)/\lambda < 0.90 \text{ \AA}^{-1}]$, but marginally larger values at higher momentum transfer. This effect is explained from the nature of the scattering operator. As $F(q)$ can be written as a Fourier transform of the charge distribution, variations in the inner regions of the charge distribution affect mainly the outer region of $F(q)$ and vice versa.

In the final nonrelativistic calculation all possible single and double excitations were included, with the following configurations included in expansion (7):

$$3d^7, \quad 3d^64s, \quad 3d^64d, \quad 3d^54s^2, \quad 3d^54p^2, \\ 3d^54d^2, \quad 3d^54f^2, \quad 3d^54s4d, \quad 3d^54p4f, \quad (13)$$

as well as all possible configurational functions. The corresponding atomic scattering factors are presented in entry D of Table 2. The change in the scattering factor is negligible.

The next stage of our investigation was the inclusion of the LS dependent relativistic effects. These additional terms are the one-electron operators for the mass-correction and Darwin terms, the two-electron operators for the two-body Darwin term, the spin-contact term and the orbit-orbit interaction. For a definition of these relativistic terms, we refer the reader to the paper by Glass and Hibbert (1978). The expansion coefficients $\{c_i\}$ were determined by diagonalizing the Hamiltonian matrix (including the LS dependent relativistic effects listed above, as well as the nonrelativistic terms) with respect to the radial functions basis determined in Section 3.

The atomic scattering factors were evaluated and the results are presented in entries B, C and D of Table 3. Comparing the 'relativistic-corrected' atomic scattering factors with the corresponding nonrelativistic factors, it is seen that the former are larger at smaller momentum transfers, but marginally smaller at higher momentum transfers [$(\sin \frac{1}{2}\theta)/\lambda > 0.90 \text{ \AA}^{-1}$].

Table 3. 'Relativistic-corrected' atomic scattering factor $F(q)$ for Co III (see Section 4)

$(\sin \frac{1}{2}\theta)/\lambda (\text{\AA}^{-1})$	B	C	D	E*
0.00	25.0000	25.0000	25.0000	25.000
0.05	24.7224	24.7200	24.7201	24.716
0.10	23.9272	23.9184	23.9188	23.904
0.15	22.7146	22.6976	22.6982	22.673
0.20	21.2177	21.1930	21.1939	21.164
0.25	19.5714	19.5414	19.5423	19.516
0.30	17.8910	17.8588	17.8595	17.845
0.40	14.7465	14.7175	14.7178	14.743
0.50	12.1591	12.1386	12.1383	12.207
0.60	10.2006	10.1882	10.1877	10.203
0.70	8.7921	8.7858	8.7853	8.917
0.80	7.8038	7.8013	7.8009	7.948
0.90	7.1062	7.1060	7.1057	7.257
1.10	6.1887	6.1901	6.1900	
1.30	5.5225	5.5238	5.5239	
1.50	4.9162	4.9172	4.9173	
1.70	4.3359	4.3365	4.3366	
1.90	3.7967	3.7970	3.7971	
2.10	3.3170	3.3172	3.3173	

* From Doyle and Turner (1968).

In Table 3 the relativistic Hartree-Fock atomic scattering factors evaluated by Doyle and Turner (1968) using the relativistic Hartree-Fock wavefunctions of Coulthard (1967) are presented in entry E. Comparing our results with those of Doyle and Turner, it is seen that for $(\sin \frac{1}{2}\theta)/\lambda \leq 0.25 \text{ \AA}^{-1}$ our nonrelativistic Hartree-Fock result is in very good agreement with the relativistic Hartree-Fock result. For the range $0.30 \leq (\sin \frac{1}{2}\theta)/\lambda \leq 0.60 \text{ \AA}^{-1}$ our 'relativistic-corrected' atomic scattering factors calculated using the 'first-order' wavefunction, the configurations being Hartree-Fock plus those representing single excitations from Hartree-Fock, are in very good agreement with the corresponding relativistic result. However, for $(\sin \frac{1}{2}\theta)/\lambda > 0.60 \text{ \AA}^{-1}$ the agreement between our results and the relativistic Hartree-Fock result is disappointing.

Although expected that one-electron excitations should have a significant effect on the atomic scattering factor, Tables 2 and 3 show that the scattering factor changes with the inclusion of two-electron excitations. In Table 4 we have separated the effects of the replacement of different Hartree-Fock orbitals by correlation orbitals at $(\sin \frac{1}{2}\theta)/\lambda = 0.40 \text{ \AA}^{-1}$, where the maximum change occurs. The contribution to the atomic scattering is given, each row representing the additional contribution to the form factor as a result of the new replacement up to and including that specified on the row. It is seen that there is an important contribution from the two-electron excitation $3d^2 \rightarrow nd^2$, being about one-third of that from the one-electron excitation $3d \rightarrow nd$. Since the atomic scattering factor is a one-electron operator, this is surprising because

such configurations have no interactions with the Hartree–Fock configuration (which alone has a large coefficient). A closer inspection of the wavefunction reveals that the inclusion of these pair correlations changes the coefficients of the single-replacement configurations, resulting in the change to $F(q)$.

One purpose of the present work was an investigation of how the atomic scattering factor changes as more configurations are included in the atomic wavefunction, in order to improve the total energy of the ground state of the atomic ion. In Table 5 the contribution to the correlation energy is given, each row representing the additional contribution to the correlation energy as a result of the new replacement up to and including that specified on the row. It is seen that the correlation energy determined using the configurations listed in (13) is approximately twice the correlation energy determined using the configurations from (12), whilst the difference in the atomic scattering factor calculated using either (12) or (13) is negligible.

Table 4. Contribution to the atomic scattering factor from the different replacements for Co III

The results are for calculation D and $(\sin \frac{1}{2}\theta)/\lambda = 0.40 \text{ \AA}^{-1}$

Replacement	Nonrelativistic	Including relativistic effects
None	0.00000	0.00000
3d → 4s	0.00000	0.00000
3d → 4d	0.06360	0.07398
3d ² → 4s ²	-0.00037	-0.00041
3d ² → 4p ²	-0.00128	-0.00133
3d ² → 4d ²	-0.02520	-0.02823
3d ² → 4f ²	0.00156	0.00142
3d ² → 4s4d	-0.00015	-0.00016
3d ² → 4p4f	0.00000	0.00000
Total contribution	0.03817	0.04529

Table 5. Contribution to the correlation energy for Co III

The results are for calculation D and the energies are in atomic units

Replacement	Nonrelativistic	Including relativistic effects
None	0.0	0.0
3d → 4s	0.00000	0.00000
3d → 4d	0.00606	0.00762
3d ² → 4s ²	0.00071	0.00074
3d ² → 4p ²	0.00465	0.00471
3d ² → 4d ²	0.08293	0.08247
3d ² → 4f ²	0.06741	0.06744
3d ² → 4s4d	0.00114	0.00116
3d ² → 4p4f	0.00001	0.00001
Total contribution	0.16291	0.16465

5. Conclusions

We have shown that using a 'first-order' wavefunction, with Hartree–Fock configurations plus those representing single excitations from Hartree–Fock, can 'over estimate' the importance of relaxing the constraints imposed by the Hartree–Fock

approximation. As we observed in the previous section, by adding two-electron excitations such a correlation has a major influence in modifying the weightings of the configurations involved in the 'first-order' wavefunction. Our results thus show the importance of incorporating all types of electron correlation systematically.

It is widely assumed that for closed-shell atoms, Hartree-Fock wavefunctions are of sufficient accuracy for evaluating atomic scattering factors. There has however been some question as to whether this is true in general, but from the results presented here it would appear that it is also true for an atomic ion with an open-shell ground-state configuration.

According to Øverbø (1977), for heavier atoms with $Z \geq 20$ the relativistic effects become important and atomic scattering factors evaluated using nonrelativistic Hartree-Fock wavefunctions are inaccurate even at small momentum transfers. From the results presented here we conclude that, for $Z = 27$, relativistic effects are not important and that for all practical purposes exclusion of relativistic effects will not result in an inaccurate evaluation of an atomic scattering factor at small momentum transfer.

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