Generalized X-ray scattering factors. Simple closed-form expressions for the one-centre case with Slater-type orbitals.

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A method for evaluating in closed form the Fourier transform of a product of two atomic orbitals, *i.e.* the so-called generalized scattering factor, is described for the case where both atomic orbitals are centred on the same atom.

The Fourier transform of a product of two atomic orbitals is called a 'generalized scattering factor'. These have been studied by Stewart (1969) who uses the notation:

$$X_{\mu\nu}(S,R) = \int \chi_\mu^* \chi_\nu \exp(iS \cdot r) dr. \tag{1}$$

Here χ_μ and χ_ν are atomic orbitals which may be localized either on the same atom or on different atoms. In the two-centre case, where the atomic orbitals χ_μ and χ_ν are centred on different atoms, the generalized scattering factors $X_{\mu\nu}$ are functions of the internuclear separation vector R as well as the scattering vector S. In this note, however, we shall consider only the one-centre case, and thus the $X_{\mu\nu}$'s discussed here will depend only on S. Let the atomic orbitals have the form:

$$\chi_{nl_\mu} = R_{nl}(r)\gamma_{l_\mu}(\theta,\varphi) \tag{2}$$

where the γ's are real spherical harmonics:

$$\gamma_s = \frac{1}{(4\pi)^{1/2}}, \quad \gamma_{p_x} = \left(\frac{3}{4\pi}\right)^{1/2}\frac{x}{r}, \quad \gamma_{p_y} = \left(\frac{3}{4\pi}\right)^{1/2}\frac{y}{r},$$

$$\gamma_{p_z} = \left(\frac{3}{4\pi}\right)^{1/2}\frac{z}{r}, \quad \gamma_{d_{xy}} = \left(\frac{15}{4\pi}\right)^{1/2}\frac{xy}{r^2}, \quad etc. \tag{3}$$

Then, when the factor $\exp(iS \cdot r)$ is expanded in terms of complex spherical harmonics and spherical Bessel functions:

$$\exp(iS \cdot r) = 4\pi \sum_{l=0}^{\infty} i^l j_l(Sr) \sum_{m=-l}^{l} Y_{lm}^*(\theta,\varphi) Y_{lm}(\theta_s,\varphi_s), \tag{4}$$

we obtain:

$$X_{\mu\nu} = 4\pi \sum_{l''=0}^{\infty} i^{l''} f_{l''}(S) O_{l''}(\gamma_{l'\mu}\gamma_{l\nu}) \tag{5}$$

where

$$f_{l''}(S) \equiv \int_0^\infty dr\, r^2 j_{l''}(Sr) R_{n'l'}(r) R_{nl}(r) \tag{6}$$

Table 1. $J_{N,k}(S,Z) = \int_0^\infty r^N \exp(-Zr) j_k(Sr) dr$

N				
3				$\dfrac{48S^3}{(S^2+Z^2)^4}$
2			$\dfrac{8S^2}{(S^2+Z^2)^3}$	$\dfrac{48S^2 Z}{(S^2+Z^2)^4}$
1		$\dfrac{2S}{(S^2+Z^2)^2}$	$\dfrac{8SZ}{(S^2+Z^2)^3}$	$\dfrac{8S(5Z^2-S^2)}{(S^2+Z^2)^4}$
0	$\dfrac{1}{(S^2+Z^2)}$	$\dfrac{2Z}{(S^2+Z^2)^2}$	$\dfrac{2(3Z^2-S^2)}{(S^2+Z^2)^3}$	$\dfrac{24Z(Z^2-S^2)}{(S^2+Z^2)^4}$
	1	2	3	4 $k \rightarrow$

and

$$O_{l''}(\gamma_{l'\mu}\gamma_{l\nu}) \equiv \sum_{m''=-l''}^{l''} Y_{l''m''}(\theta_s,\varphi_s) \int d\Omega\, Y_{l''m''}^* \gamma_{l'\mu}\gamma_{l\nu}. \tag{7}$$

In (5) and (7), $O_{l''}$ is a projection operator which acts on the angular function $\gamma_{l'\mu}\gamma_{l\nu}$ and annihilates all the function except those portions which transform according to the angular momentum quantum number l''. Acting on the first few angular functions which we can construct from the real spherical harmonics given in (3), these projection operators yield:

$$O_0(\gamma_s\gamma_s) = \frac{1}{4\pi}$$

$$O_1(\gamma_s\gamma_{p_\mu}) = \frac{\sqrt{3}}{4\pi}\frac{S_\mu}{S}$$

$$O_0(\gamma_{p_\mu}\gamma_{p_\nu}) = \frac{\delta_{\mu\nu}}{4\pi} \tag{8}$$

$$O_2(\gamma_{p_\mu}\gamma_{p_\nu}) = \frac{3}{4\pi}\left(\frac{S_\mu S_\nu}{S^2} - \frac{\delta_{\mu\nu}}{3}\right),$$

all other contributions being zero. The properties of projection operators of this kind acting on tensor functions have been discussed by Avery & Cook (1974). Combining (5) and (8), we obtain:

$$X_{s,s} = f_0$$

$$X_{s,p_\mu} = \sqrt{3}i\frac{S_\mu}{S}f_1 \tag{9}$$

$$X_{p_\mu,p_\nu} = \delta_{\mu\nu}f_0 - 3\left(\frac{S_\mu S_\nu}{S^2} - \frac{\delta_{\mu\nu}}{3}\right)f_2.$$

Thus, for example, according to (9) and (6),

$$X_{p_x,p_y} \equiv \int \chi_{n'p_x}\chi_{np_y} \exp(iS \cdot r) dr$$

$$= -3\frac{S_x S_y}{S^2}\int_0^\infty dr\, r^2 R_{n'1}(r)R_{n1}(r)j_2(Sr) \tag{10}$$

where j_2 is a spherical Bessel function of order 2.

In the case of Slater-type orbitals, the radial functions R_{nl} can be written in the form:

$$R_{nl}(r) = \sum_j C_j r^{n_j-1} \exp(-\zeta_j r) \tag{11}$$

and therefore the radial factors $f_{l''}(s)$ of (6) can be expressed in terms of integrals of the type:

$$J_{N,k}(S,Z) \equiv \int_0^\infty r^N \exp(-Zr) j_k(Sr) dr. \tag{12}$$

[Our notation here has been chosen to conform with that of Stewart (1969), except that we denote the integrals by $J_{N,k}(S,Z)$ instead of $S_{N,k}(S,Z)$.] Stewart gives an expression for integrals of this type in terms of a hypergeometric series. On the other hand Harris & Michels (1967) and Harris (1973) have shown that these integrals can be evaluated in closed form. Starting with

$$J_{1,0} = \frac{1}{S^2 + Z^2} \tag{13}$$

and using the recursion relations (derived from the properties of spherical Bessel functions)

$$J_{v+1,v} = \left(\frac{2vS}{S^2 + Z^2}\right) J_{v,v-1}$$

$$J_{v+2,v} = \frac{(2v+2)Z}{(S^2 + Z^2)} J_{v+1,v} \tag{14}$$

$$(S^2 + Z^2)J_{\mu+1,v} + (\mu + v)(\mu - v - 1)J_{\mu-1,v} = 2\mu Z J_{\mu v}$$

$$SJ_{\mu,v-1} + (\mu - v - 1)J_{\mu-1,v} = Z J_{\mu v},$$

we obtain the integrals listed in Table 1. With the help of these integrals, the scattering factors can be expressed in closed form. Thus, for example, suppose that the radial functions of (10) are given by

$$R_{n'1} = \frac{(\zeta')^{5/2}}{2\sqrt{6}} r \exp\left(-\frac{\zeta'r}{2}\right)$$

$$R_{n1} = \frac{(\zeta)^{5/2}}{2\sqrt{6}} r \exp\left(-\frac{\zeta r}{2}\right). \tag{15}$$

Then, using (12) and (10), together with Table 1, we obtain:

$$X_{p_x,p_y} = \frac{-3(\zeta'\zeta)^{5/2}(\zeta' + \zeta)S_x S_y}{\left[S^2 + \left(\frac{\zeta' + \zeta}{2}\right)^2\right]^4}. \tag{16}$$

In many applications, the expressions given by Stewart (1969) may be the most useful. However, in some applications the simple closed-form expressions discussed here may also prove to be of value.

References

AVERY, J. S. & COOK, M. (1974). *Theor. Chim. Acta*, **35**, 99–112.

HARRIS, F. E. (1973). *Computation Methods in Quantum Chemistry*. Preprint, Quantum Chemistry Group, Uppsala Univ., Uppsala, Sweden.

HARRIS, F. E. & MICHELS, H. H. (1967). *Advanc. Chem. Phys.* **13**, 205–266.

STEWART, R. F. (1969). *J. Chem. Phys.* **51**, 4569–4577.