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Form factors for core electrons useful for the application of quantum crystallography (QCr) to organic molecules

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Form factors are calculated for the core electrons of the first-row atoms B, C, N, O and F. The form factors are presented in an analytical form, as appears in *International Tables for X-ray Crystallography* [Ibers & Hamilton (1974), Vol. IV, pp. 103–145. Birmingham: Kynoch Press; present distributor Kluwer Academic Publishers, Dordrecht]. Having such form factors for the core electrons reduces the number of parameters to be determined by the methods of quantum crystallography (QCr). It is shown that the form factors obtained are quite accurate. Thus, when they are used in QCr, they are expected to be consistent with accurate charge densities.

1. Motivation and results

Quantum crystallography (QCr) combines crystallographic information with quantum-mechanical calculations (Massa *et al.*, 1995). In our QCr applications, we use molecular orbitals, a single Slater determinant and a density matrix which is a projector to define a quantum-mechanical model. The connection between that model and experimental crystallographic data is made through the electron-density distribution. Fourier transforms of the density are made to agree closely with their experimental analogs, namely, structure-factor magnitudes obtained from X-ray scattering measurements. The procedure used includes least-squares adjustment of elements of a projector density matrix to optimize the fit to the experimental structure-factor magnitude data. The method is carried out in a way that preserves the projector and normalization properties of the density matrix.

Studies of this general type have shown that quantum-mechanical information can be generated from X-ray data. For example, we have applied QCr methods to the study of maleic anhydride (Huang *et al.*, 1999), obtaining Mulliken population analysis of the charge distribution, which tracks well the analogous Mulliken population analysis results obtained independently from Hartree–Fock calculations. In the maleic anhydride study, we found it to be very useful to separate the contribution to the scattering of the core electrons and the valence electrons. In this way, the number of basis functions required in the quantum model for maleic anhydride was much reduced. This has the valuable practical effect of increasing the ratio of data used to least-squares parameters adjusted. Removal of the core-electron scattering from that part of the problem represented by molecular orbitals, however, generates the need for a separate expression for the core-electron scattering. We constructed such expressions in analytical form and, for C and O, used them to advantage in the case of maleic anhydride.

The core form factors are given as

$$f((\sin\theta)/\lambda) = \left\{\sum_{i=1}^{4} A_i \exp[-B_i(\sin^2\theta)/\lambda^2]\right\} + C. \tag{1}$$

The sum of Gaussians is the form in *International Tables for X-ray Crystallography* (Ibers & Hamilton, 1974). Nine parameters, $\{A_i, B_i, i = 1\text{–}4\}$ and C reproduce the core form factors. These are determined for each atom type by least-squares fitting to the respective form factors, tabulated in *International Tables for X-ray Crystallography* for 56 different values of $(\sin\theta)/\lambda$. The value of the least-squares parameters are given in Table 1.

Thakkar & Smith (1992) correctly point out that the parameter C in (1), were f to be Fourier transformed, would correspond to an unphysical Dirac δ function component in the density. In their work, they therefore prefer to eliminate the parameter C. However, we have chosen to carry the parameter C, simply in order to conform to the usage adopted in *International Tables*.

When the parameters, given in Table 1, are used in equation (1), one may calculate the form factors for the same 56 values of $(\sin\theta)/\lambda$ as appear in Table 2.2D of *International Tables for X-ray Crystallography* (1974), Vol. IV, pp. 103–105 (Ibers & Hamilton, 1974). As can be seen by comparison of such calculated values with the corresponding entries in *International Tables*, the fit is well within the acceptable range. A summary is shown in Table 2.

As seen in Table 2, for each of the atoms considered, we calculated the residual, in addition to maximum and mean errors. One observes a range of values from 6.0×10^{-5} down to 3.1×10^{-6}. We have also listed the maximum error, the value of $(\sin\theta)/\lambda$ at which the maximum error occurs and the mean error. Clearly, the form factors are of the same quality as those 56 values listed in *International Tables*. For maleic anhydride, we used equation (1) to determine the core scattering contributions of C and O atoms for 467 different

Table 1
Coefficients related to the analytical expression for core form factors in equation (1).

	A_1	A_2	A_3	A_4	B_1	B_2	B_3	B_4	C
B (He core) 5	6.260585	0.887678	0.797078	0.163403	0.001637	0.522327	1.400067	3.198460	−6.10875
C (He core) 6	6.261320	0.890229	0.795518	0.160751	0.001618	0.345630	0.966600	2.121265	−6.10794
N (He core) 7	6.259986	0.888784	0.791351	0.168628	0.002260	0.267246	0.934512	0.188306	−6.10925
O (He core) 8	6.260308	0.889621	0.789114	0.169520	0.002579	0.195482	0.716123	0.120777	−6.10893
F (He core) 9	6.260595	0.890250	0.787361	0.170154	0.002449	0.149871	0.564412	0.087221	−6.10865

Table 2
Error measures for fits using the coefficients of Table 1.

Atom	Least-squares residual	Maximum error	$(\sin\theta)/\lambda$ (Å^{-1})	Mean error
B	3.1×10^{-6}	0.0009	2.000	0.0001
C	2.2×10^{-5}	0.0020	2.000	0.0004
N	2.5×10^{-5}	0.0016	2.000	0.0006
O	1.0×10^{-5}	0.0010	1.800	0.0004
F	6.0×10^{-5}	0.0007	1.400	0.0003

values of $(\sin\theta)/\lambda$, corresponding to the scattering data available from experiment. The final R factor obtained in that case was 1.14%, indicating a very good fit of the theoretical model to the experimental diffraction data. This occurs for reasons that include our use of a quantum-mechanical projector density matrix for the valence electrons and appropriate use of thermal factors for describing the motion of the nuclei. Moreover, a treatment of the experimental data with a view to eliminating systematic errors also proved to be important. In addition, our use of the core scattering representation described above also contributed to the good fit that was obtained. We suggest that the parameters given here are useful generally where QCr methods are applicable.

2. Discussion

There are alternative ways to determine the values of form factors at various values for $(\sin\theta)/\lambda$. On p. 487 of *International Tables for Crystallography* (1992), Vol. C, two methods are mentioned, interpolation of tabulated functions or the use of parametric equations as applied in this article. In agreement with the statement on p. 487, that equation (1) 'has been found to be particularly effective', we too have found this to be true over the range of our calculations, $0 < (\sin\theta)/\lambda < 2.0$ Å^{-1}. For higher angles, a logarithmic polynomial is presented on the same p. 487 for use in the range $2.0 < (\sin\theta)/\lambda < 6.0$ Å^{-1}. The choice of method is optional. The method that we have used in this article has been shown here to be quite reliable for application to core electrons in organic molecules. As mentioned, it has already been applied in a study of maleic anhydride with good results.

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