球状原子を仮定した散乱因子の精密化

澤田晴朗 (工学院大)

THE ESTIMATION OF THE 'OBSERVED' EXPERIMENTAL ATOMIC SCATTERING FACTORS
THROUGH HIGHLY PRECISE CRYSTAL STRUCTURE REFINEMENTS WITH X-RAY SINGLE-
CRYSTAL DIFFRACTION DATA
H.SAWADA(KOGAKUIN UNIV.)

The results brought about through relatively precise crystal structure refinements provide invaluable information such as the ionic state, thermal vibration, or the bonding character of the atoms. However, there is a difficulty encountered in the interpretation of the electron density departure from the theoretically expected often observed in the proximity of the atomic centers, even for refinements which appeared to proceed smoothly. In crystal structures of high symmetry, these electron density residuals may accompany significantly intense 'ghost' peaks at other seemingly unrelated positions. The present study reports on a novel method which well accounts for this impediment by adjusting the structural model through derivation of best-fit non-Gaussian experimental atomic scattering factors from the observed diffraction data.

The observed electron density distribution in a crystal is generally expressed as a three-dimensional Fourier series, the structure factor F 's (derived from the X-ray diffraction intensities) serving as the coefficients for the Fourier synthesis of the electron density, where the summation extends over the limited number of data acquired in the experiment. Therefore, the obtained electron density distribution more or less suffers from effects of termination of the series. In turn, summation made for the $F_o - F_c$ difference between each corresponding structure factor which was observed (F_o), and calculated (F_c) from the structural model, usually exhibits almost no or only small termination effects.

Previously exercised methods in determining experimental scattering factors were based on Fourier summation of F_o , therefore required a large number of observed data. To satisfy this condition, the missing term values are filled in with calculated ones and the effects of the unobservable terms are numerically corrected for series termination. In contrast, the presently discussed procedure functions through minimizing the sum $\sum(F_o - F_c)$ for all observed (reliable) structure factors. Thus the results are believed to be comparatively unbiased by any particularly presupposed structural model, that is, other than sphericity of the atom.

Although the sphericity of the electron density distribution of static atoms is assumed throughout this procedure, departure of the radial distribution from a Gaussian function-type is permitted. This follows from consideration that the theoretically calculated scattering factors are based on a free atom, therefore, should be different for atoms in a crystalline state with a crystal (ligand) field erected about them. By adjusting for the deviation of the radial distribution from Gaussian, the $F_o - F_c$ difference becomes chiefly attributable to asphericity of the electron density distribution around the atoms.

Application of this method drastically reduces the $F_o - F_c$ discrepancy in the radial electron density distribution (as anticipated), leaving intact the inherently aspherical residuals. Comparison of the crystallographic R -values (R -factors) with the results from related works employing other kinds of methods shows that despite of the relative simplicity in scheme of the present procedure, the outcome of refinements with this method are for most cases better than those for previous studies.