

Removing residual bond density in organic molecules using simplified virtual atoms: a technical note

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The Independent Atom Model (IAM) is based on assumption that the electron density is well described by the spherically averaged density of the isolated atoms. It is a good estimate for the atoms for which the valence electron density is a minor part of the total. IAM is less successful for light atoms: when the quality of structure is reasonably good, you can see areas of bond-related residual positive density located on C-C, C-N and C=O bonds. With resolution better than 0.6-0.5 Å, these peaks can be higher than 0.4 e/Å³; R-factor and goodness of fit are abnormally large. Controversially, this discourages high resolution measurements!

To reduce the bias coming from bond density, we employ an empirical approach using usual IAM software (SHELXL-201X, Jana2006). Scattering centers are placed at fixed calculated positions between C, N, and O atoms, with 'occupancies' being different for single, double, aromatic and triple bonds. Scattering is approximated by a single Gaussian which can be possibly justified by a small value of correction. These 'atoms' are treated as isotropic: multiplication of scattering Gaussian by Debye-Waller factor yields one Gaussian function to describe both effects. The number of introduced parameters can be as low as one (for overall occupancy of pseudo-atom part of the structure). Introduction of virtual atoms makes the effect similar to one hydrogen atom per 4-5 C-C bonds, which is significant enough to justify the effort. Alternatively, each bond can be treated separately (number of additional parameters is roughly equal to the number of bonds). This leads to further improvement. An attempt was made to handle C-H bonds and lone pairs in the same fashion.

A number of structures of various organic and element-organic molecules were tested. Visible improvement of fitting characteristics was achieved, especially for molecules with aromatic fragments. Some representative examples: Biphenyl, resolution 0.57 Å, before correction R=0.059, after 0.036. Diphenylacetylene, 0.58 Å: before correction R=0.048, S=1.04; after R=0.026, S=1.02. Dimethyl-3,4,5,6-tetraphenylcyclohexa-3,5-diene-1,2-dicarboxylate, 0.80 Å, Cu radiation (!): before R=0.035, S=1.04; after R=0.026, S=1.03. *trans*-[3-(3-nitrophenyl) oxiran-2-yl](phenyl)methanone, 0.58 Å: before R=0.046, after 0.032. Ylide, 0.48 Å: before R=0.027, after 0.018. Uncertainties of bond distances are also visibly lower. This enable us to remove most of residual bond density from the Fourier difference map allowing then to address other sources of deviation such as disorder and, of course, experimental and data processing limitations.