

Stepping back to go forward: the invariom approach towards intermolecular interactions

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Electron density studies from X-ray diffraction proved to be very helpful in addressing many important chemical problems in modern material and bio-sciences. Despite progress in experimental techniques, equipment and theoretical background, efforts are still being made to go beyond small ordered molecules with excellent reflective power. Among other options, a concept of invarioms (aspherical atomic scattering factors computed for an atom in a given covalent environment within the multipole formalism) has been recently introduced. This database approach allows quickly constructing an “experimental” electron density distribution from X-ray diffraction data, including those of a low (normal) resolution, collected with copper radiation and/or for larger molecules with poor reflective power and suffering from a disorder. A resulting electron density reproduces features of covalent bonds and describes well those of hydrogen bonds, as obtained from a full multipole refinement against high-resolution datasets. While the invariom approach is applicable to any organic compound (as missing invarioms may be easily calculated), it still needs to be pushed beyond molecular crystals formed by H-bonds with one symmetry-independent molecule in a unit cell ($Z'=1$), for which it has been mostly used so far, to make it more widespread.

We tested the performance of the invariom approach on a series of organic compounds featuring intermolecular interactions from classic H-bonds to weak van-der-Waals contacts, having more than one distinct species in a crystal and giving X-ray diffraction data that suffers from experimental pitfalls other than listed above. Although being based on pseudo-atoms derived from isolated molecules and thus not taking crystal environment into account, the invariom approach was shown to provide an adequate description of intermolecular interactions in crystals governed by H-bonds (as in 1,10-phenanthroline hydrate) and even better one for those formed by weak van-der-Waals contacts (as in s-tetrazine). Although ignoring charge redistribution between chemically or symmetrically distinct species, the invariom approach results in chemical bonding features in molecular systems with $Z'>1$ (such as 1,10-phenanthroline hydrate, $Z'=3$) and even in ionic crystals (such as guanidinium salts) that are amazingly similar to those obtained from electron density study based on high-resolution X-ray diffraction or periodic quantum chemistry.

Despite the inherent limitations and earlier unknown but easy to resolve issues with atoms at special positions (as usually is the case of ionic crystals) and species with strong delocalization of electron density, the invariom approach is a good choice if the above two options are not applicable or are too cumbersome. Moreover, as some frequently encountered problems with X-ray diffraction data (such as twinning) are not always recognized if their contribution is very low (while their negative effect is not), this approach may be even used (in addition to Hirshfeld test or transferability indices) to judge the quality of an electron density distribution obtained by conventional multipole refinement of high-resolution datasets. The invariom approach thus emerges as a useful tool for exploring intermolecular / interionic binding (a least for organic compounds and if it is not extremely strong) and so the properties of many crystalline materials.

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