Poster

The effect of (not) applying symmetry constraints during refinement and using different local coordinate systems on local symmetry of atoms and atom types in the MATTS data bank

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In the MATTS data bank[1,2], the local coordinate system and symmetry are essential parts of an atom type definition, specified manually when adding a new atom type entry. The local coordinate system and local symmetry for an atom type can be different than the local coordinate systems and local symmetry constraints used during the refinement of individual atoms from model molecules. There is also a possibility of not using local symmetry constraints during the refinement at all. We found out that applying or not applying symmetry constraints can change symmetry for atoms, which may result in different preferred symmetry for an atom type. Moreover, we often can see higher symmetry than specified in the MATTS data bank.

Proper local coordinate system orientation is crucial for assigning atom types to atoms in molecules and creating new atom types, as it preserves atomic electron density symmetry when multipole model parameters are averaged. While orienting the local coordinate systems, as many first neighbors as possible should be engaged, especially the ones considered as symmetry-equivalent. The choice and orientation of the local coordinate system can change the multipole model parameters, causing some of them to vanish. According to the rules[3], each point symmetry group has its own set of allowed and not-allowed site-symmetric spherical harmonics. Not-allowed ones should have multipole populations equal to 0. By comparing these rules with multipole model parameters generated by our rotation of local coordinate systems for atoms in model molecules (noteworthy, we do not enforce any local symmetry higher than 1), we can discover symmetry for each atom (pseudosymmetry when a none-zero threshold is used to find vanishing multipoles). We can also see which symmetry elements are present, how they are oriented, which neighboring atoms are equal to one another from the perspective of analyzed atom and then atom type, and which local coordinate systems are preferred to directly observe symmetry elements and point groups.

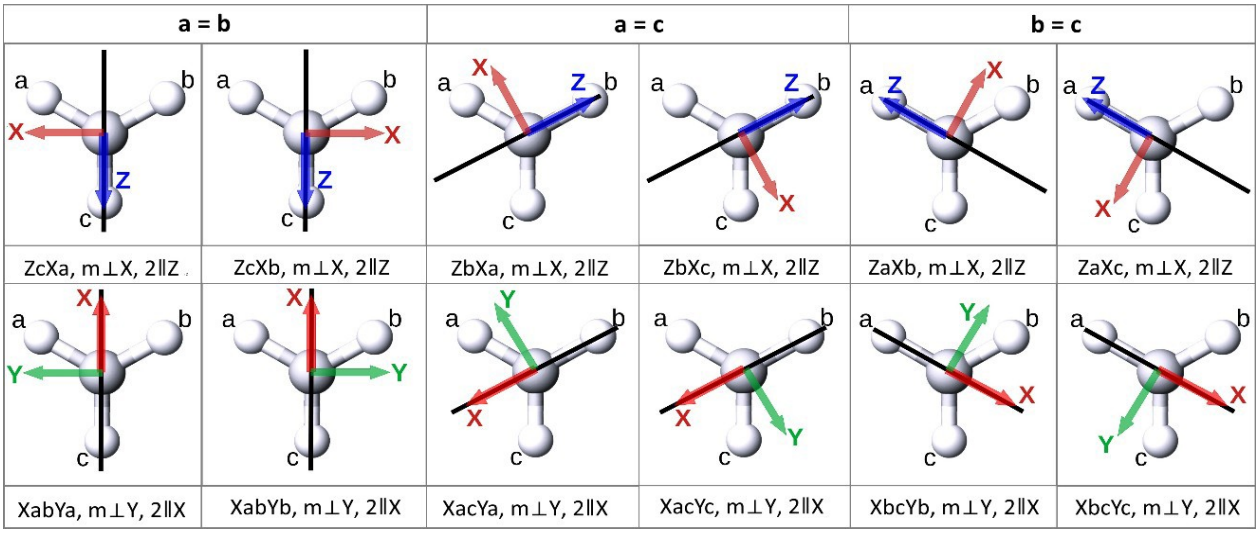

Figure 1. Symmetry elements observable in different local coordinate systems for planar atoms with 3 neighbors (a, b, c). Possible point symmetry groups are: $\bar{6}m2$, *mm*2, or *m*. Because the group is planar, at least *m* symmetry is always present. The *mm*2 symmetry is seen when two neighbors are the same (a = b, a = c, or b = c). The $\bar{6}m2$ symmetry is seen when all 3 neighbors are the same (a = b = c), so all symmetry elements are present as shown above.

[1] Jha, K.K., Gruza, B., Sypko, A., Kumar, P., Chodkiewicz, M.L., Dominiak, P.M. (2022). *J. Chem. Inf. Model.*, **62**, 3752-3765.

[2] Rybicka, P.M., Kulik, M., Chodkiewicz, M.L., Dominiak, P.M. (2022). *J. Chem. Inf. Model.*, **62**, 3766-3783.

[3] Kuorki-Suonio, K. (1977). *Isr. J. of Chem.,* **16**, 115-123.

This research was funded by National Science Centre, Poland UMO-2020/39/I/ST4/02904.