Poster

The influence of wave function’s basis set on the fit of multipole model to wave function

V.Ignatev[1], P.Dominiak[1]

[1]*Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089, Warsaw, Poland*

v.ignatev@uw.edu.pl

The Multipolar Atom Types from Theory and Statistical clustering (*MATTS*) databank [1, 2] is an advanced tool which applies Transferable Aspherical Atom Model (*TAAM*) [3] for crystal structures refinement. Such a method helps to describe the asphericity of atomic electron densities and helps to interpret diffraction data better than refinement approaches based on spherical atoms approximation.

The generation of MATTS data can be briefly described as follows: calculation of wave functions of experimental geometries of the molecules, generation of structure factors by analytical Fourier transform of wave functions and multipole refinement of generated structure factors. The features of the wave function used in our approach have a significant impact on resulting multipole model. That is why in this study we decided to investigate, how the wave function’s basis set size will influence the charge density quality of multipole model fitted to wave function.

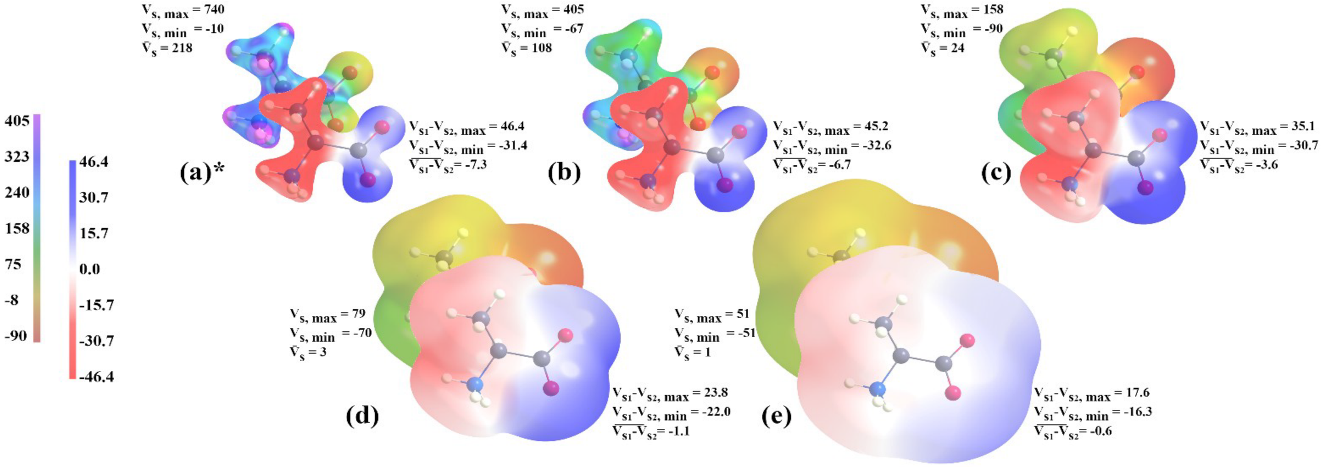

Figure 1. Iso-density surfaces of L-alanine with reference electrostatic potential (**background**) and with difference between reference electrostatic potential and electrostatic potential of multipole model based on Def2TZVP basis set mapped on it (**foreground**) (iso-density surfaces values: **a** – 0.1 a.u., **b** – 0.05 a.u., **c** – 0.01 a.u., **d** – 0.001 a.u., **e** – 0.0001 a.u.; electrostatic potential values are given in kcal/mol; $\mathbf{V}_{s,max}$, $\mathbf{V}_{s,min}$ and $\bar{\mathbf{V}}_s$ denote maximum, minimum and average electrostatic potential values on a given surface; *for 0.1 a.u. surface positive electrostatic potential values are truncated to 405 kcal/mol)

We examined a number of basis sets from different families (6-31G**, Def2SVP, Def2TZVP, cc-pVDZ-PP/cc-pVDZ, cc-pVTZ-PP/cc-pVTZ and UGBS1P) within the B3LYP DFT functional framework. In order to evaluate the multipole’s model charge density quality, we compared resulting multipole model and wave function based on UGBS1P basis set (the reference) using charge density related parameters. For this purpose, we used correlation between electrostatic potentials, atomic electron populations, electrostatic potential values averaged over molecular surfaces and crystallographic R-factors as parameters for comparison.

The results of the study show that switching from double-zeta to higher-zeta basis sets within our approach has a positive impact on multipole model’s charge density.

[1] P. M. Rybicka, et. al., (2022), *J. Chem. Inf. Model.*, 62, 16, 3766–3783. doi:10.1021/acs.jcim.2c00145

[2] K.K. Jha, et al., (2022), *Journal of Chemical Information and Modeling* 62 (16), 3752-3765. doi:10.1021/acs.jcim.2c00144

[3] J. M. Bąk, et al., (2011), *Acta Crystallographica Section A Foundations of Crystallography, 67(2), 141–153.* doi:10.1107/s0108767310049731

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