N-representable one-electron reduced density matrix refinement at finite temperatures

Sizhuo Yu, Jean-Michel Gillet

SPMS, CentraleSupélec, Université Paris-Saclay, Paris, France

sizhuo.yu@centralesupelec.fr

Electron density matrices and wave functions are central objects of study in quantum crystallography. Recent advances have shown that, beyond conventional charge density refinement, a one-electron reduced density matrix (1-RDM) satisfying N-representability conditions can be reconstructed using jointly experimental X-ray structure factors (XSF) and directional Compton profiles (DCP) by means of semi-definite programming [1, 2, 3]. An experimentally derived 1-RDM can be considered as a direct quantum description of electrons in crystals and could serve as a reference for theoretical calculations. In order to assess the robustness of the method, we have performed a 1-RDM model refinement for crystalline urea ($CO(NH_2)_2$) using both static (0K) and dynamic (50K) pseudo-experimental data. In the latter case, the refinement procedure includes deconvolution of nuclei thermal motion effect. Such a procedure allows for a more realistic comparison between experimental and ab-initio 1-RDM . To achieve refinement on such a molecular crystal, symmetry constrained were introduced and core electrons contributions were kept frozen (see figure 1). Additionally, we have examined the impact of data quality on the refined 1-RDM. We aim to showcase the method's robustness against realistic experimental situations and and its potential for extension to larger periodic non-molecular systems.

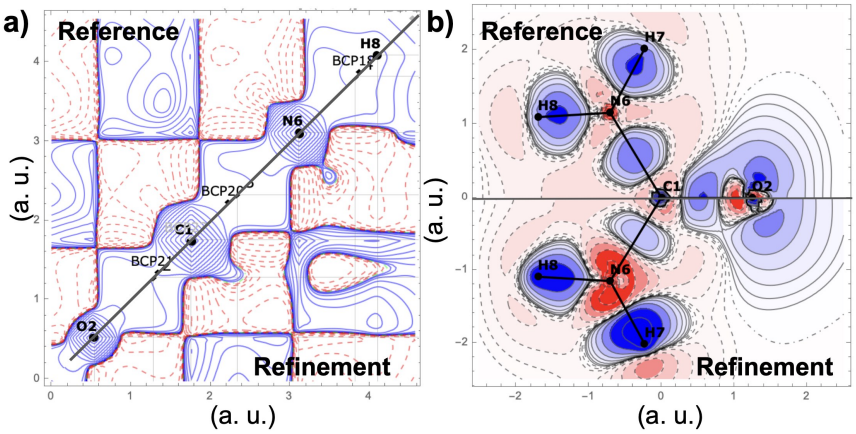

Figure 1: a) the reference (upper left) and refinement (lower right) 1-RDM $\Gamma(x, x')$ on the $O-C-N-H$ bond path. b), the reference (top) and refinement (bottom) deformation density in the molecular plane. Positive (blue) and negative (red) contours are drawn on a logarithmic scale (0.01×2^n e/Å^3). The refinement result is obtained from structure factors ($\frac{\sin\theta}{\lambda} < 1$ Å^{-1}) and 8 directional Compton profiles ($\Delta q = 0.2$ a.u.) generated from the reference density functional theory calculation with a B3LYP functional and a cc-pVTZ basis set under 50K.

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[2] Saber Gueddida, Zeyin Yan, and Jean-Michel Gillet. “Development of a joint refinement model for the spin-resolved one-electron reduced density matrix using different data sets”. In: *Acta Crystallographica Section A* 74.2 (Mar. 2018), pp. 131–142. DOI: 10.1107/S2053273318000384. URL: https://doi.org/10.1107/S2053273318000384.

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