

Crystallography meets orbital-free DFT – two-pronged approach towards chemical bonding characteristics in chemical bonding analysis

Anna Krawczuk*

Georg-August University Goettingen, Tammannstr. 4, Goettingen, 37077, Germany. *Correspondence e-mail: anna.krawczuk@uni-goettingen.de

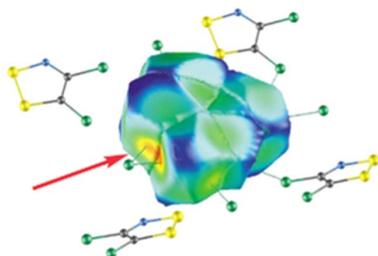
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As solid-state chemists, one of our principal aims is to understand which forces determine three-dimensional build-up of a crystal structure and which intermolecular interactions are at the origin of chemical, physical or biological responses of the studied materials. We are particularly interested in identification of reproducible structural features which are transferable among different systems. This leads to better comprehension of molecular self-assembly processes promoting specific crystal packing and thus the prominent properties at the molecular and/or macroscopic level. One of the very promising routes towards rational design of materials is the combination of well established quantum chemical calculations with experimental electron density-based techniques within the framework of the recently reinvigorated field of Quantum Crystallography (QCr; Genoni *et al.*, 2018; Genoni & Macchi, 2020). On the one hand, such a fusion between experiment and theory allows extraction of fundamental information on the nature of chemical bonding. On the other hand, the quantification of observable properties significantly increases the amount of available data on structural features of a solid state and decreases the level of uncertainty. It also provides a means of comparison of experimental findings with theoretical benchmark calculations, significantly improving robust and powerful methods optimized to rapidly screen and investigate crystalline materials with non-negligible properties of a bulk and correlate those findings with structural features.

The recent work of Bartashevich *et al.* (2021) fits well under the umbrella of modern QCr methods. It refers to an earlier article on the orbital-free quantum crystallography (OF-QCr; Tsirelson & Stash, 2020) approach which, guided by quantum mechanical calculations, employs information obtained from high-resolution X-ray diffraction experiments to assess forces and potential in a crystalline state. Electronic forces, observed in a crystal, are expressed by kinetic and DFT potentials and are further defined in terms of experimental electron density and its derivatives.

Up to now, the OF-QCr approach was tested on purely covalent or ionic structures, such as diamond or NaCl. In the current work, the authors focus on a more challenging compound where apart from purely covalent bonds, a variety of non-trivial intermolecular interactions, including C—Cl···Cl and C—Cl···S types, are present. Appel's salt (C₂Cl₂NS₂⁺·Cl⁻) (Appel *et al.*, 1985; Rabe & Müller, 1999), as it is referred to, is a representative of 1,2,3-dithiazole systems, which are proven to be precursors for obtaining stable radical salts upon dimerization (Hicks, 2010; Rakitin, 2011). Interestingly, bonding properties of the salt itself were so far described only in terms of bond lengths and calculated electronic properties (Konstantinova *et al.*, 2016); there had been no previous studies based on experimental electron density distribution, which is the focus of the discussed paper by Bartashevich *et al.* (2021).

As mentioned earlier, the OF-QCr model takes advantage of the potential and forces derived from experimental electron density, rather than from quantum-chemically-derived energies. That gives a unique opportunity to observe bonding features from a different perspective than the one offered by other quantum topology methods, for example Quantum Theory of Atoms in Molecules (QTAIM; Bader, 1995), the most widely used partitioning scheme. The most appealing is the comparison of the electrostatic potential $\varphi_{\text{ESP}}(\mathbf{r})$ (ESP) distribution of the cation in Appel's salt with two functions strictly extracted using the OF-QCr approach, namely a potential acting on an electron in



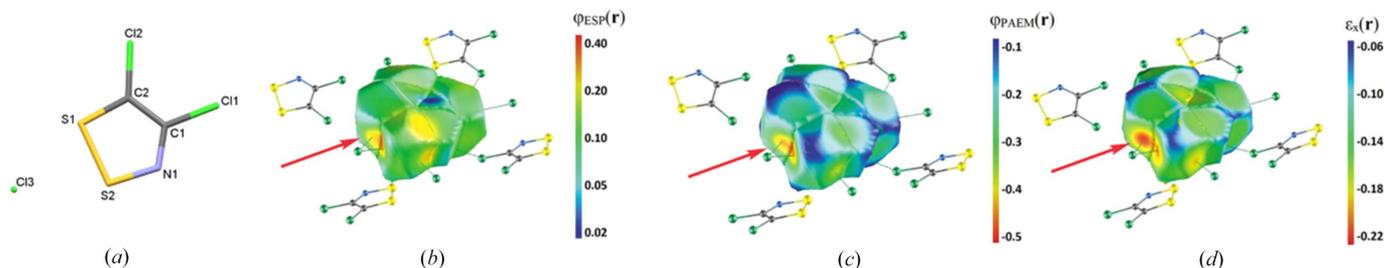


Figure 1

(a) Appel salt structure; (b) electrostatic potential $\varphi_{\text{ESP}}(\mathbf{r})$; (c) potential acting on an electron in a molecule $\varphi_{\text{PAEM}}(\mathbf{r})$; (d) exchange energy density per electron $\varepsilon_x(\mathbf{r})$. All quantities are mapped on zero-flux surface (ZFS) of experimental electron density. Red arrow points at electrophilic site near the centre of S—S bond, bond paths are marked with thin green lines. [Views *b*, *c* and *d* are reprinted with permission of the International Union of Crystallography, from Bartashevich *et al.*, 2021.]

a molecule $\varphi_{\text{PAEM}}(\mathbf{r})$ (PAEM) and exchange energy density per electron $\varepsilon_x(\mathbf{r})$. PAEM, unlike classical ESP, apart from considering already realized electrostatic interactions includes information on electronic exchange and is defined as follows: $\varphi_{\text{PAEM}}(\mathbf{r}) = -\varphi_{\text{ESP}}(\mathbf{r}) + \varphi_x(\mathbf{r})$ (Bartashevich & Tsirelson, 2018). In addition, it can be directly derived from experimental electron density distribution. Nonetheless, in case of Appel's salt, the same conclusions can be drawn considering the electrophilic and nucleophilic properties of the system. Both quantities pinpoint the most electrophilic sites located near the centre of the S—S bond, suggesting the absence of a σ -hole (Politzer & Murray, 2019) as an extension of a covalent bond (see regions marked with red arrows in Fig. 1 (reproduced from Bartashevich *et al.*, 2021)). Moreover, the traces of slightly less electrophilic sites are also observed in the area of chalcogen bonds, exactly as expected for such kinds of interactions (Kolář & Hobza, 2016).

A rather different picture is drawn when one analyses the exchange energy density per one electron, $\varepsilon_x(\mathbf{r})$ [see Fig. 1(*d*)]. Near the centre of S—S bond, instead of one distinct minimum, as observed for PAEM, two well separated minima are identified. These 'exchange channels' correspond very well to the existence of two chalcogen bond paths S1...Cl3 and S2...Cl3 identified with the QTAIM approach. Neither ESP, nor PAEM, can grasp this subtle yet non-negligible change caused by non-covalent interactions. This shows the advantage of exchange energy density over both potentials, especially when one aims at identification and accurate description of rather strong, non-covalent interactions such as chalcogen or halogen bonds.

With the present results, Bartashevich *et al.* (2021) showed that the recently proposed orbital-free quantum crystallography scheme can be successfully applied to describe non-covalent interactions and extract information not available via energy-derived electrostatic potential. The benefits of OF-

QCr are synergistically enhanced when combined with QTAIM, allowing a more complete view of chemical bonding in a crystalline state than either approach could achieve alone. This opens new routes towards finding connections between the quantum topological approaches and the way in which materials function. The potential symbiotic relationship formed by these two approaches will help guide the design of new materials by reverse crystal engineering tools (Macchi, 2014) with more specificity towards non-trivial intermolecular interactions.

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