

Characterizing the halogen and chalcogen bonds in crystals: PAEM vs ESP

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We examined the features of the electrostatic potential (ESP) and the potential acting on an electron in a molecule (PAEM) [1, 2]. Unlike the ESP, the PAEM contains both classic and quantum components. For analysis of the halogen and chalcogen bonding features, the considered functions were mapped on the different sides of the closed RDG isosurface [3] placed between non-covalently interacting atoms. We found that on the side of the electron-donor atom, the region of non-covalent interactions is characterized by the potential acting on an electron, and on the side of the σ -hole it is described by the electrostatic potential acting on the unit positive charge [4].

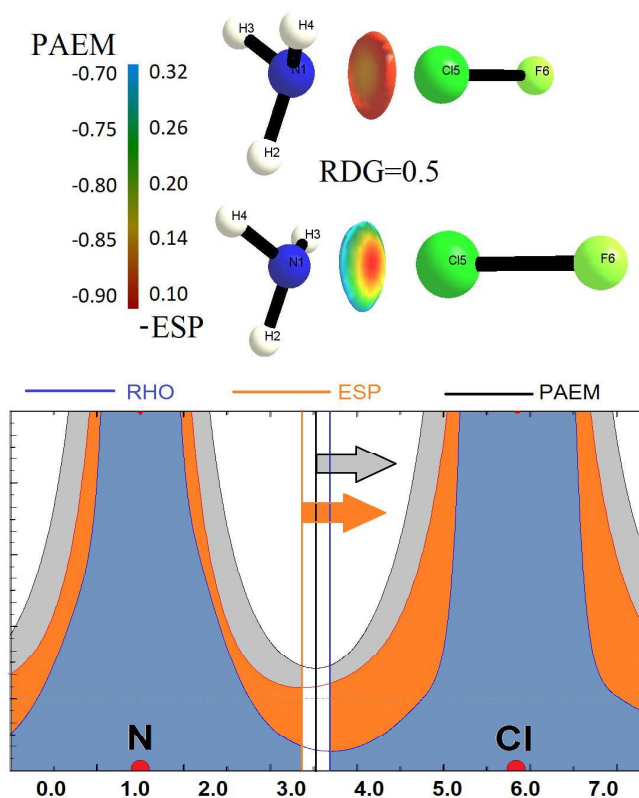


Fig. 1 Distributions of $-ESP$ and $PAEM$ mapped on the isosurface of $RDG = 0.5$ and 1D functions along the halogen bond $N\dots Cl$ in the complex $NH_3\dots ClF$

Thus, a combination of these tools is proposed for the halogen and chalcogen bonding identification. Moreover, a comparison of the distributions of these functions on the isosurface of the electron density (ED) for the halogen and chalcogen atoms carried out. The account for the exchange-correlation interaction in PAEM retains the specific anisotropy of the electrostatic

potential, which is commonly used for explanation the halogen bonding with reliance on σ -hole concept. Along the halogen bonds, the curvatures of -ESP and PAEM functions are opposite: from the electron donor atom ESP increases more steeply, while from the halogen atom the sharper increase is observed for PAEM function. The functions -ESP and PAEM mapped on the closed isosurface of the reduced density gradient significantly differ from the side facing the halogen atom and from the side, looking at the electron donor atom. The relative positions of $-ESP^{\max}$ and $PAEM^{\max}$ functions along the halogen bond line help to distinguish which atom is the halogen bond donor, and which is the acceptor, while the values of $PAEM^{\max}$ correlate with the electron delocalization indices.

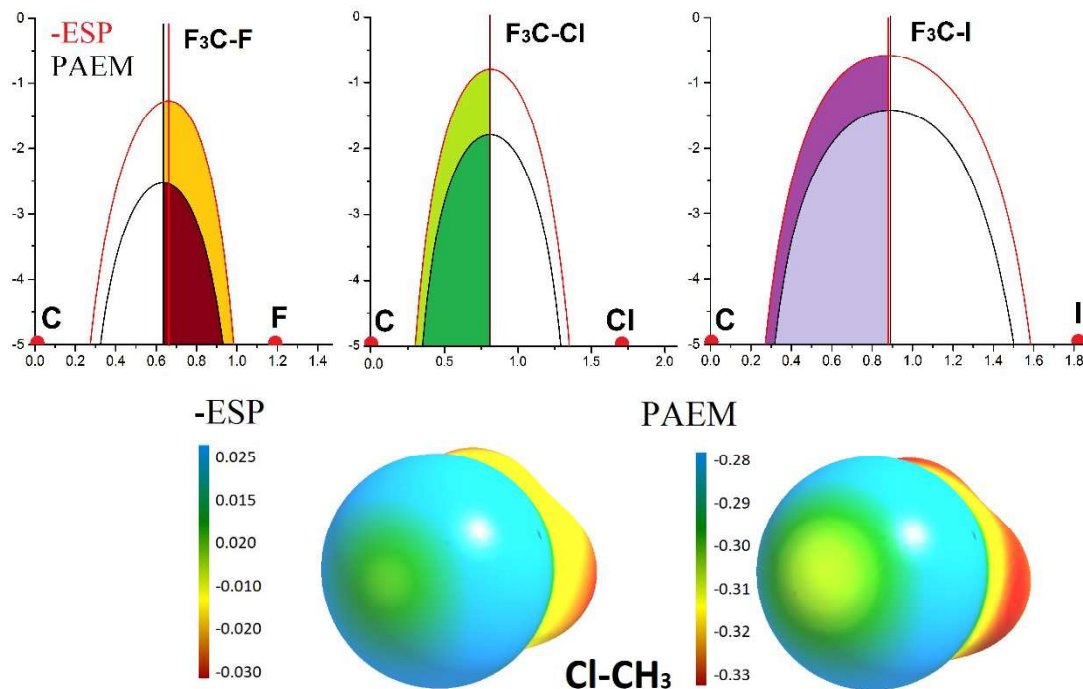


Fig. 1 Distributions of – ESP and PAEM mapped on the isosurfaces of $ED=0.001$ a. u., for ICI, BrCl, Cl₂, ClF molecules

In crystals, the typical non-covalent halogen and chalcogen bonds accompanied by the complicated mutual orientations of anisotropic features of the halogen/chalcogen atoms. The standard geometrical criteria are not enough to distinguish the type of bonding and to recognize which atom is a donor or which is an acceptor of electrons in such cases. A methodology that suggests the use of -ESP and PAEM functions jointly copes with this problem successfully.

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