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Cluster analysis of functional group polarizabilities

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The charge density distribution of a functional group is predominately determined by the nuclei and bonding pattern composing the functional group and by its close environment, whereas the rest of the molecule plays a smaller role. Since many functional group properties can be directly related to the charge density, it is not surprising that they retain similar characteristics even if the rest of the molecule is different. The properties are thus indicative for a particular group and furthermore, they are transferable among different molecules. This is not only true for the ground state electron density but also for the polarizability and consequently for many important electrostatic and dielectric properties. Our study focuses on distributed polarizabilities of functional groups, which are obtained by partitioning of the molecular electron density into atomic contributions using the quantum theory of atoms in molecules (QTAIM) [1]. We defined a local coordinate system for each functional group and expressed the polarizability tensors with respect to this system to make them fully self-contained and thus transferable. The local coordinate system is based on the inertia tensor of the functional group; its three principal axes define the axes of the local coordinate system. Other researchers [2,3] have calculated distributed polarizabilities of functional groups based on different methods. However, they have not defined any subcategories for the functional groups and thus the close environment has not been taken into account. Our goal is to group molecules containing a given functional group into clusters based on the polarizability tensor. Two different unsupervised clustering algorithms were used, k-means and an agglomerative hierarchical clustering. Generally, the algorithms are able to produce chemically intuitive clusters. The cluster means can be used as representative functional group polarizabilities for the molecules in a given cluster and as building blocks to calculate the polarizability of other molecules that do not belong to the original clustering dataset. This allows to rapidly estimate polarizabilities of large molecules and, together with the dipole moment, to approximate the crystal field and therefore the dielectric properties of a crystalline material.

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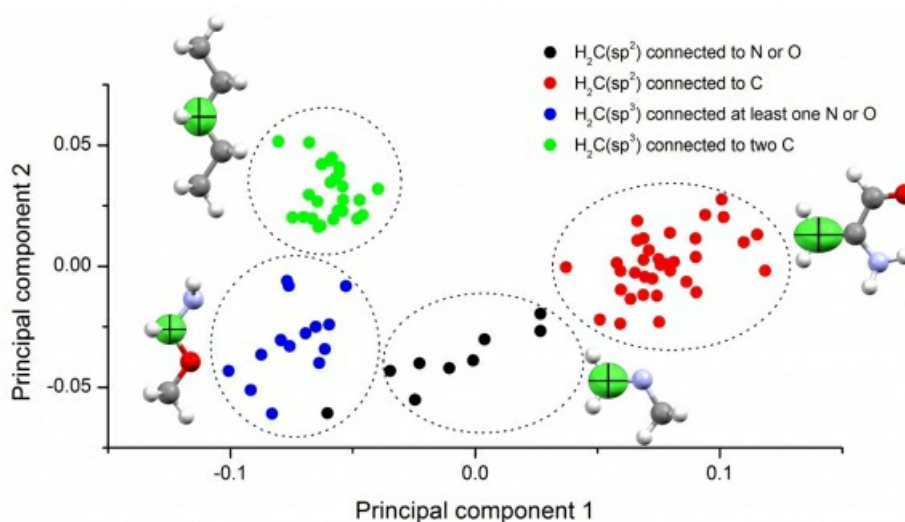
The CH_2 functional group polarizabilities of 110 molecules are shown in principal component space. K-means was used to classify them into four clusters. An exemplary molecule is shown for each cluster with the symmetrized CH_2 polarizability tensor in green.

Keywords: distributed polarizability, dielectric properties, cluster analysis