

A novel approach for the study of intermolecular interactions: molecular deformation densities

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Abstract. A new method to study intermolecular interactions via direct electron density measurements has been proposed. This approach involves the sum of constituent molecular electron densities as a reference rather than the usual sum of spherical atom densities for the evaluation of deformation densities. One may thus be able to focus specifically on the regions involving dominant intermolecular interactions such as hydrogen bonding, charge transfer, etc.

Keywords. Electron density; intermolecular interactions.

During the last two decades, reliable electron density measurements have become possible (Coppens 1982) due to development of x-ray instrumentation and better computational facilities. On the other hand, advances in quantum chemical methods have made it possible to theoretically compute these electron densities very accurately. The experimentalists normally report the maps of atomic deformation density (ADD) defined by

$$\Delta\rho(\mathbf{r}) = \rho_{\text{mol}}(\mathbf{r}) - \sum_{\text{Sph. atoms}} \rho(\mathbf{r}). \quad (1)$$

The spherical (sph.) atom densities in (1) are normally extracted from Hartree-Fock theoretical wavefunctions. These ADD do not highlight the accumulation of charge in the intermolecular regions since the major contributions to $\Delta\rho(\mathbf{r})$ as defined by (1) come exclusively in the proximity of the nuclei and from the bond regions. The intermolecular interactions are better monitored if the spherical atom concept is replaced by a constituent molecule or fragment formalism.

Let us consider two interacting molecules *A* and *B* and define the molecular deformation density (MDD) as

$$\Delta\rho(\mathbf{r}) = \rho_{\text{mol}}(\mathbf{r}) - \{\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})\} \quad (2)$$

Here, $\rho_{\text{mol}}(\mathbf{r})$ is obtained from an accurate x-ray diffraction experiment. The constituent molecular densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ can be obtained theoretically. These calculations can be carried out at various levels of accuracy by using standard software, say the set of GAUSSIAN programs. A good starting point for these computations could be at a 6-31 G level. A more elaborate DCI or higher-level CI calculation can also be taken up, if necessary. The geometries of the species *A* and *B* are to be frozen as they exist in the supermolecule *AB*. In fact, the atomic co-ordinates in *AB* may be supplied by a high-order x-ray refinement from the above experimental data themselves. Thus the MDD

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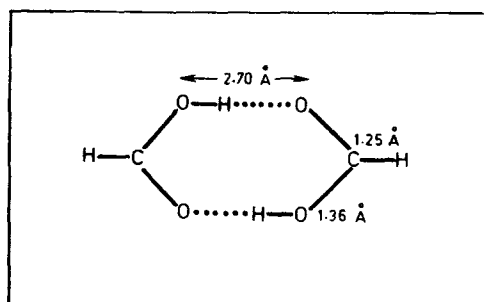


Figure 1.

defined via (2) are not marred by the features dominant around the atomic sites, but truly reflect the intermolecular interactions.

As an example, consider the classic case of the formic acid dimer (see figure 1). The experimental molecular electron densities for the dimer may be obtained by accurate x-ray diffraction studies (Coppens 1982). A calculation on the formic acid monomer in the dimer geometry (also obtained from the above experimental data) is then to be performed employing an extensive basis-set. The MDD's extracted thereby are expected to reveal the features of hydrogen bond in a more specific manner, i.e. they will not be wiped out by the otherwise dominant atom-centered functions. The molecular deformation densities would thus yield valuable information on hydrogen-bonded systems, charge-transfer complexes, etc. Exploratory studies outlined above, are currently being carried out on boric and formic acids.

An alternative approach based exclusively on the experimental data can also be developed. This involves the concept of molecular scattering factors in place of their atomic counterparts in the evaluation of monomer densities. However, a suitable shape function in terms of the centre of the mass of the molecule is needed to account for the thermal effects. It appears to us that this approach would be considerably more tedious than the one described earlier.

In conclusion, it is felt that a better approach for a systematic study of intermolecular interactions indeed needs to be developed. It is hoped that the above methodology based on molecular deformation densities provides one.

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Reference

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