

# Correlation between Materials Properties and Accurate Electron Densities: Distributed Polarizabilities of Amino Acids and their Aggregates

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To rationally design optical materials, distributed atomic polarizabilities of amino acids and their hydrogen-bonded aggregates are calculated and the functional groups able to build-up the largest electric susceptibilities in crystals are identified. The breakdown of total polarizabilities into atomic contributions is useful because a given property may originate from one particular functional group. In this respect, the transferability of atomic properties allows exporting group quantities, calculated with high accuracy in small molecules, to systems that would be too expensive to calculate *ab initio*. Among several schemes, we adopted the “atomic response theory”,<sup>1</sup> based on the topological partitioning of the electron density within the QTAIM, which has been implemented in the *PolaBer* program.<sup>2</sup> To rationalize optical properties of the solid state, the so-called cluster method have been employed, where the polarizability of several interacting molecules are evaluated as a whole, just like in standard molecular calculations. When associated with a partitioning scheme, the polarizability of a molecule embedded in the cluster can be extracted and used to estimate the susceptibility of a periodic system. By comparing the polarizabilities of the isolated molecule and that from the molecular cluster, one gains insight into the role of short and medium-range intermolecular interactions, crucial for the design of optical materials.

In this work, the QTAIM distributed polarizabilities of amino acids and their aggregates are calculated at different levels of theory in order to propose a quality- and cost-oriented protocol for the evaluation of optical properties. Having highly correlated coupled-cluster, configuration interaction and  $MP_n$  results obtained with extremely large, complete basis-sets as benchmark, we were able to find the most efficient theoretical schemes, which usually combine a long-range corrected hybrid DFT functional and a sufficiently diffuse correlation-consistent basis-set. In view of these results, we have chosen the CAM-B3LYP/d-aug-cc-pVDZ level of theory to investigate the transferability of optical properties in the amino acid series and the effect of intermolecular interactions on such properties.

Our results demonstrate a very good transferability of the functional group polarizabilities, enabling to identify the groups that contribute the most to the global susceptibility of materials based on amino acids. In particular, we found that the  $C_\alpha$  atom provides a rather large optical density. In keeping with experimental evidence, another highly active group is the aromatic ring, which is also quite anisotropic (a feature to be carefully considered in the case where low or high birefringence is desirable). On the other hand, the sulfur atom, although quite polarizable, does not produce a very large molar refraction, because its atomic basin has a large volume. However, sulfur plays the role of enhancing the polarizabilities of all neighboring atoms, therefore, contributing indirectly to increase the overall crystal refraction. The transferable functional groups can be used to estimate the susceptibility of a material without carrying out a full quantum-mechanical calculation; tested cases show good comparison with experimental values.

Our analysis also suggests that a proper quantum-mechanical treatment of the first coordination sphere in amino acid aggregates is necessary to estimate the effects of mutual polarization between the molecules. Local field approximations overestimate the polarizabilities of molecules in aggregation because they do not take into account the volume contraction when going from gas-phase to condensed matter. However, local field theories in the more sophisticated distributed functional group model are clearly more adequate than in the point dipole approximation.

Finally, the strategy outlined in this work is an effective tool for the rational design of optical materials because it enables reasoning in terms of transferable functional groups and the effects of the intermolecular interactions on them.

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<sup>1</sup> Keith, T. A. In *The Quantum Theory of Atoms in Molecules*; Matta, C. F.; Boyd, R. J.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007, pp 61-94.

<sup>2</sup> Krawczuk, A.; Pérez, D.; Macchi, P. *PolaBer*: a program to calculate and visualize distributed atomic polarizabilities based on electron density partitioning. *J. Appl. Cryst.* **2014**, *47*, 1452-1458.