

REDUCED-SCALING AND ACCURATE PREDICTION OF MOLECULAR RESPONSE PROPERTIES

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Modern electronic structure approaches facilitate unprecedented predictions of molecular and materials properties in complex systems. Specifically, energy decomposition analysis (EDA) has been remarkably helpful at informing intuitive interpretations of the molecular driving forces behind chemical phenomena such as non-covalent and covalent bond formation.

We present a generalization of energy decomposition analysis (gEDA) for the analysis of molecular response properties such as polarizabilities [1]. The gEDA approach analyzes the interplay between molecular moieties in terms of chemically intuitive contributions to the observable response property, such as inter-fragment polarization or charge delocalization. These insights enable us to develop an intuitive interpretation of the molecular response to external stimuli and their interplay with the molecular environment.

Moreover, exploiting the fragment-localized formulation enables us to develop expedited predictive models as required for predictions on large systems. To this end, we partition the response properties into long-range ("global") electrostatic contributions that are handled efficiently and accurately using methods such as the continuous fast multipole method, and short-range ("local") charge-transfer contributions for which we exploit sparsity, when present, to achieve reduced computational scaling.

We present applications of energy decomposition analysis in the interpretation of ultrafast vibrational spectroscopy to monitor carbon capture in ionic liquids and for the expedited computational prediction of dielectric polymers.

References

- [1] D. S. Lambrecht, *Computational and Theoretical Chemistry*, **2019**, 1149, 24-30.

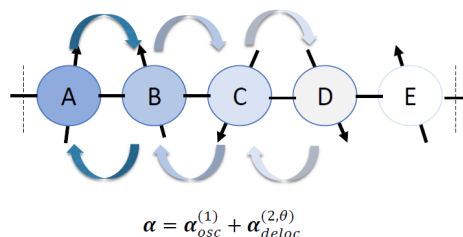


Fig. 1. Hybrid global/local model to partition the polarizability into electrostatic long-range and a charge-transfer local components. Components are handled separately to reduce computational scaling while preserving accuracy (e.g. fast multipole for electrostatics and block-sparse matrix algebra for charge-transfer).

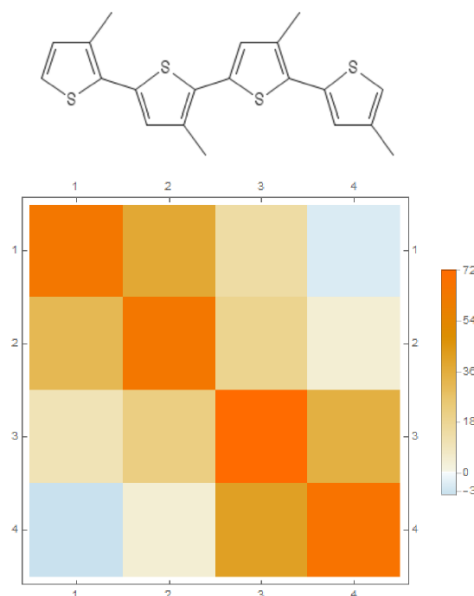


Fig. 2. Sparsity of the charge-transfer component to the static polarizability in tetra(methyl thiophene). Each block represents one monomer and data is shown in atomic units.