The Mysteries of Chirality, Solvation, and Optical Activity

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AThe optical properties of chiral molecules are among the most challenging to predict and simulate — even for state-of-the-art quantum chemical methods — because of their delicate dependence on a variety of intrinsic and extrinsic factors, including electron correlation, basis set, vibrational/temperature effects, etc.[1, 2] In numerous studies over the last decade, we have demonstrated the importance of advanced quantum chemical methods such as coupled cluster response theory for the prediction of an array of gas-phase chiroptical properties such as optical rotation angles, circular dichroism rotatory strengths, Raman optical activity scattering intensity differences, and more[3]. The primary disadvantage of such methods, however, is their high-degree polynomial scaling, which limits significantly the size of system to which they may be applied. Furthermore, solvation makes the task even more difficult, not only dramatically expanding the complexity of the simulation, but sometimes altering even the sign of the chiral response. It is thus essential that we reduce the computational demands of the more accurate and reliable quantum chemical methods. In this lecture, we will discuss recent efforts in our group toward this goal, including the exploration of local correlation techniques[4], many-body expansions for the description explicitly solvated systems[5], a variety of implicit solvation models[6], frozen-virtual natural orbitals for reduction of the correlation space[7], and real-time dynamics.

References:

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