Development of effective stochastic potential method using random matrix theory for efficient conformational sampling of molecular quantum mechanical properties at non-zero temperatures

Jeremy Scher and Ari Chakraborty
Department of Chemistry, Syracuse University, USA

The relationship between structure and property is central to chemistry and enables the understanding of chemical phenomena and processes. Need for an efficient conformational sampling of chemical systems arise from the presence of solvents and the existence of non-zero temperatures. However, conformational sampling of structures to compute molecular quantum mechanical properties is computationally expensive because a large number of electronic structure calculations are required. In this work, the development and implementation of the effective stochastic potential (ESP) method is presented to perform efficient conformational sampling of molecules. The overarching goal of this work is to alleviate the computational bottleneck associated with performing a large number of electronic structure calculations required for conformational sampling. We introduce the concept of a deformation potential and demonstrate its existence by the proof-by-construction approach. A statistical description of the fluctuations in the deformation potential due to non-zero temperature was obtained using infinite-order moment expansion of the distribution. The formal mathematical definition of the ESP was derived using functional minimization approach to match the infinite-order moment expansion for the deformation potential. Practical implementation of the ESP was obtained using the random-matrix theory method. The developed method was applied to calculate quasiparticle gap, exciton binding energies, and excitation energies of solvated CdSe clusters at 300K. The need for large sample size to obtain statistically meaningful results was demonstrated by performing 10^5 ESP calculations. The results from these calculations demonstrated the efficacy of the ESP method for performing efficient conformational sampling. We envision that the fundamental nature of this work will not only extend our knowledge of chemical systems at non-zero temperatures but will also generate new insights for innovative technological applications.