Anisotropic van der Waals dispersion interactions using TD-DFT

Jason N. Byrd, John A. Montgomery, Jr., and Robin Côté

Department of Physics, University of Connecticut, Storrs, CT 06269

The calculation of non-covalent interactions of highly polarizable molecules is an outstanding problem in chemistry and physics. Difficulties arise both in accurate treatments of dispersion interactions between molecules and in the evaluation of surfaces of sufficient size for use in further computations. This is complicated by the fact that in low densities, cold gas reactions are very sensitive to the long range behavior of the molecular interaction. While "gold-standard" calculations using coupled cluster theory with singles, doubles and perturbative triples provides a reliable method for evaluating interactions the computational cost involved more than a few points of an interaction surface becomes prohibitive for even medium sized molecules. Expanding the long range interaction into a van der Waals series reduces the cost of evaluating a surface to the computation of a few parameters.

We have implemented the sum over states approach to calculating van der Waals coefficients using time dependent density functional theory up order R^{-6} including anisotropic contributions. In recent calculations using several widely used density functions we have demonstrated accurate dispersion interactions for the highly polarizable alkali diatoms. In this work we have extended the previous sum over states implementation to arbitrary non-linear molecular structures. Using a semi-classical Langevin model dependent on the van der Waals interaction between two molecules to describe the reaction process, it is possible to provide estimates on the reaction rate. We employ this model with our calculated van der Waals coefficients to examine the reaction rates of a sample of molecules important to interstellar chemistry in the tens of Kelvin regime.