

Long-Range Forces between Small Polar Molecules

The interactions between small molecules are often described using an expansion in spherical harmonics with coefficients that are functions of the centre-of-mass separation. While this in principle provides a complete description, it offers little opportunity for understanding and it may fail to converge at physically interesting distances.

An alternative approach is to describe separately the electrostatic, induction and dispersion terms that emerge from perturbation theory. Convergence difficulties may be overcome by using an atom–atom or site–site description. In this way it is easy to obtain an accurate description of the electrostatic interaction, which generally dominates for polar molecules. However, induction and dispersion make important contributions, and a simple but accurate description is needed. A method for obtaining such a description from *ab initio* calculations will be described.