

Abstract: Reliable prediction of the structure and stability of molecular crystals and their polymorphs is essential for understanding their properties and potential applications. However, obtaining reliable binding energies of molecular solids requires using high level electronic structure methods and strict convergence with numerical parameters. This becomes particularly challenging for molecular solids with many atoms in the unit cell, where calculations can become prohibitively expensive for high levels of theory, such as coupled clusters with singles, doubles, and perturbative triples (CCSD(T)). In this thesis, we focus on the development and assessment of approximate theoretical methods for calculation of binding energies and use four high-dispersion solids as test systems: ethane, ethylene, and orthorhombic and cubic forms of acetylene. To begin, we compare the efficiency of periodic boundary conditions (PBC) and many body expansion (MBE) approaches in calculating the binding energy of the considered systems. We discuss in detail how difficult it is to reach converged binding energy values with respect to the numerical parameters and then compare the results obtained from both approaches. In the remaining part of the thesis, we use the MBE results to examine the accuracy of random phase approximation (RPA) and Møller-Plesset (MP) perturbation theory in describing individual contributions and total binding energy of the considered systems by comparing them with reference CCSD(T) data. Additionally, we show how the accuracy of RPA can be affected by the orbital inputs used for the calculations. We find that RPA with additional corrections is promising, and its accuracy depends on the individual contributions and orbitals considered. Finally, we examine the accuracy of the proposed correction scheme, which can be used to obtain reference binding energies of the considered systems at a lower cost than the CCSD(T) method.

Keywords: Molecular solids, binding energy, periodic boundary conditions, many body expansion, random phase approximation