Accurate Evaluation of Intermolecular Potentials and Properties

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Interaction potentials and properties play a main role in many physical and chemical phenomena and are the subject of a considerable number of experimental and theoretical studies. Weak intermolecular complexes are characterized by an interaction dominated by dispersion, interaction that is essential in processes like the solvation or adsorption of molecules. Taking into account the high accuracy of the experimental results available, the computational study of the dispersion interaction is challenging and difficult, as not only large basis sets, but also high-level correlation methods are mandatory in order to compete with the experiments.

We evaluate accurate potentials and properties in weak intermolecular complexes, using the coupled-cluster singles and doubles (CCSD) and the CCSD including connected triples (CCSD(T)) models and large basis sets extended with sets of midbond functions.[1] We obtain ground and excited state intermolecular potential energy surfaces and calculate the bound states. We compare the results with those of previous theoretical studies and the experimental data available, improving considerably the former, getting a very good agreement with the latter, and in some cases being able to correct and complete the experimental assignments. Results for the ground state of the benzene-Ar, naphthalene-Ar,[2] CO-Ar,[3] HCCH-He,[4] and the CO-N_2 complexes will be presented.

With the CCSD response theory we evaluate interaction induced (hyper)-polarizabilities and the corresponding virial coefficients. Results for the CO-Ar complex will be shown.[5]

References

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