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Computation of Accurate Intermolecular Potentials and the Spectra of van der Waals Molecules

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Significant progress has recently been made in the accurate calculation of intermolecular potentials. This progress is based on the computer implementation of the expressions for the various interaction energy components derived by symmetry adapted perturbation theory (SAPT) [1]. The effects of intramolecular electron correlation on these components are taken into account [2] through double-perturbation theory or SAPT combined with coupled cluster theory. Further improvement is achieved by the computation of high-quality long-range coefficients from correlated monomer multipole

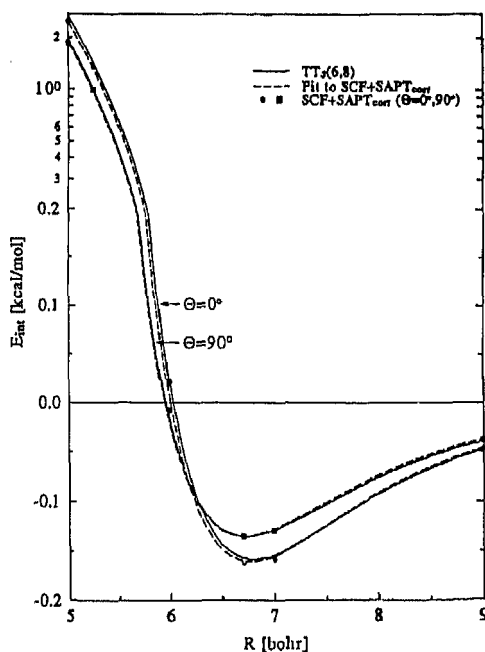


Fig. 1. Ar-H₂ interaction potential computed by SAPT (points and dashed line) and accurate semi-empirical calculations (solid line) for $\theta = 0^\circ$ (linear) and 90° (T-shaped).

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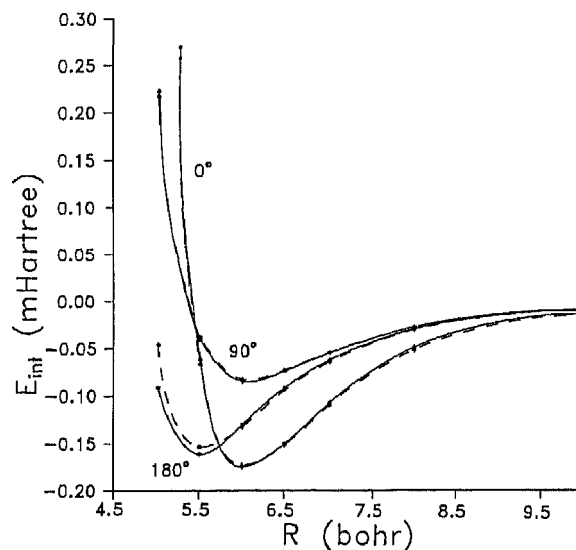


Fig. 2. He-HF interaction potential computed by SAPT (solid line) and accurate semi-empirical calculations (dashed line) for $\theta = 0^\circ, 90^\circ$ and 180° , with the HF bond length $r = 1.7328$ bohr.

moments and (frequency dependent) polarizabilities [3]. The accuracy of the intermolecular potentials thus obtained is illustrated on the examples of Ar-H₂ [4] and He-HF [5], see Figs. 1 and 2. It can be checked by exposing these potentials to the severe test of computing the (observed) spectra of these van der Waals molecules [6,7].

In the second part of this talk some new results were presented for the (NH₃)₂ dimer, where the calculation of the vibration-rotation-tunneling states and the spectroscopically observed quantities from a given intermolecular potential is a major computational effort in itself [8]. Various model potentials which resemble the incomplete and different *ab initio* potentials available have been investigated. Comparison with the spectroscopic data leads to interesting conclusions about the origin and the characteristics of the hydrogen bonding in this complex [9,10].

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