AN EFFECTIVE AND ACCURATE CALCULATION OF VIBRATIONS FOR FOUR ATOM MOLECULES

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The challenging one wave number accuracy goal in calculating vibrational energy levels of three atom molecules has only recently been attained. This involves computationally expensive multi reference methodology with basis set extrapolation with corrections for relativistic and non-Born-Oppenheimer effects. A three-dimensional direct fit to the *ab initio* energies is used to obtain the potential energy function.

Our approach for computing the lower energy levels of centrally bound four atom molecules, which furthermore may have inversion motion, is more economical in two essential points. First, the full-dimensional potential energy function is expressed as a Taylor-type series expansion, with separate procedures for anharmonic and more harmonic motions. This expansion is reliable also further away from the equilibrium geometry, it converges fast, and it is applicable to other kinds of systems. Secondly, in the electronic structure calculations the full configuration interaction and the complete basis set limit can be effectively approached with the R12 method combined with the higher excitations in the coupled cluster series.