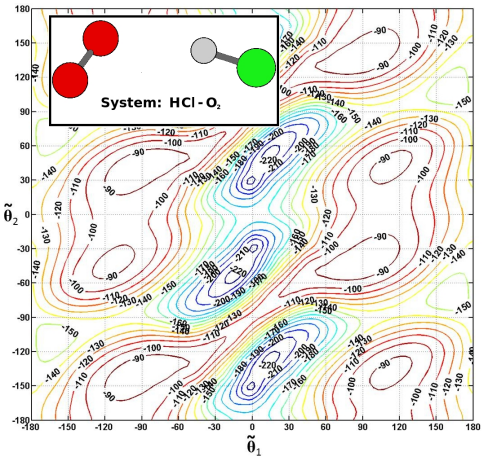
A CODE FOR AUTOMATED CONSTRUCTION OF POTENTIAL ENERGY SURFACES FOR VAN DER WAALS SYSTEMS

ERNESTO QUINTAS SÁNCHEZ, RICHARD DAWES, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*.

The potential energy surface (PES) constitutes a cornerstone for theoretical studies of spectroscopy and dynamics. We fit PESs using a local interpolating moving least squares (L-IMLS) approach.[a] The L-IMLS method is interpolative and has the flexibility to fit energies or energies and gradients, where inclusion of gradient information significantly reduces the number of points required for an accurate fit.



The method permits fully automated PES generation: beginning with an initial set of seed points, an automatic point selection scheme determines where new data are required and, in a series of iterations, computes new ab initio data and updates the fit until a specified accuracy is reached. We have interfaced this fitting approach to popular electronic structure codes such as Molpro and CFOUR to automatically generate ab initio 4D PESs for vdWs systems composed of two (rigid) linear fragments.

We present here our freely distributed code designed to run in parallel on a computing cluster, allowing the user to specify the system (masses, interatomic equilibrium distances, symmetry, energy range of interest, etc.) through an input file. For a selection of benchmark systems, we show that PESs with fitting errors below 1 cm^{-1} can be constructed using only a few hundred ab initio points.

[a] M. Majumder, S. Ndengue and R. Dawes, Molecular Physics 114, 1 (2016).