

Report of the STSM of Mr Thomas Mellor at the University of Stuttgart

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Potential energy surfaces in Different Coordinates

Guntram Rauhut's Group at the Institut für Theoretische Chemie has built a database of accurate potential energy surfaces (PES) for various polyatomic molecules. These are potentially very useful for the ExoMol group at University College London in the generation of molecular line lists. However, to maximise their utility, they would most conveniently be expressed as functions of internal coordinates such as bond lengths and angles. Currently, the PESs in this database are defined in terms of the molecular normal mode coordinates. The aim of this visit was to develop an interface between the normal mode and internal coordinates and thus to make the PES database compatible with the ExoMol computational tools (such as e.g. DVR3D and TROVE).

Prior to the visit, I had been developing a program designed for this purpose. Here, a user inputted a molecular structure, defined the coordinates, and added the potential energy surface obtained from the database. The user was then able to provide any set of internal coordinates to obtain an energy. The program was able to convert the internal coordinates into the normal coordinates, but there had been difficulties in using the database itself to obtain the correct energy.

At the start of the visit, I wanted to ensure that the transformation into normal coordinates was correct, due to the aforementioned difficulties. In fact, after I learned from the group the exact conventions they used, I discovered and corrected an error in the program in the transformation.

After this, it was established that the most sensible course of action was to utilise the newer format of potential energy surface files as their structure was simplified and they will slowly replace and populate the database over the coming years. Both Guntram and his PhD student Benjamin Ziegler explained quite thoroughly to me the structure of these files. Due to the simplification, an automated reading of the ab-initio energies was made feasible, something not practical with the older format. Thus I rewrote code that previously read fitted expansion coefficients of an H₂O test case to one that reads the ab-initio energies of any file. Reading the ab-initio energies directly instead of the expansion coefficients was done because the latter was not available from the file by default as found on the database but instead required rerunning MOLPRO with a different input. Therefore, groups without a version of MOLPRO would be able to use the database, and, in any case, this simplifies the work required of the end user.

However, reading in the ab-initio energies means that the program also has to perform the fitting, something not anticipated initially. Benjamin Ziegler developed an efficient technique for fitting the multidimensional surfaces into a weighted sum of products of one dimensional basis functions. We

decided to use polynomial functions due to their simplicity; Guntram's group had previously tested various basis functions and determined that polynomials were sufficient for the systems we were interested in. During the visit, I partially completed the fitting algorithm, but from the discussions I had with Guntram and Benjamin, I am confident I would be able to complete it successfully. We will also maintain contact to check that the obtained energies are correct.