

# Exam project: Marco Scavino

Version 1.0

## OBJECTIVE OF THE EXERCISE

Build a **Fortran 95** program to assess the consistency between two harmonic potential energy surfaces (PESs) computed at different levels of theory.

## DESCRIPTION

Vibrational spectroscopy provides detailed information on structural properties, which can be analyzed with the help of computational chemistry. The level of calculation, primarily for the electronic structure calculations, is critical to an accurate simulation of the band-shape. Depending on their quality, different methods can produce very different results. Beyond looking at the resulting spectral band-shape, detailed information can be extracted by comparing the structural changes between two levels of calculations and the changes in the curvature of the harmonic potential energy surfaces (PESs). This can be conveniently done with the affine transformation proposed by Duschinsky,

$$Q' = JQ'' + K,$$

with  $Q'$  and  $Q''$  sets of mass-weighted normal coordinates, defined with respect to the equilibrium Cartesian coordinates  $X^{\text{eq}}$ ,

$$Q^{\text{eq}} = L^T M^{1/2} X^{\text{eq}}$$

$M$  is the diagonal matrix of atomic masses and  $L$  are the eigenvectors of the Cartesian force constants matrix (second derivatives of the potential energy with respect to the Cartesian coordinates).

$J$  (dimensionless) and  $K$  (in atomic units) are respectively the Duschinsky matrix and the shift vector, defined as

$$J = L'^T \{L''^T\}^{-1}$$
$$K = L'^T M^{1/2} (X''^{\text{eq}} - X'^{\text{eq}})$$

One limitation of the Duschinsky matrix is that it is only valid for small structural changes. This will be assumed to be the case here. The transformation stands if translation and rotation are minimized, which means that the structures must be superposed and ideally in Eckart orientation.

This transformation is general and can be applied to any program, which can compute geometries and force constants. Here, the suite of quantum chemical programs GAUSSIAN will be used for reference, and more precisely the exchange file format supported by the program, the formatted checkpoint file.

## The formatted checkpoint file

The formatted checkpoint file is a file exchange format used by the suite of quantum chemical programs GAUSSIAN to facilitate migration of data between major revisions or with different programs. The data are expected in atomic units and can be mostly sorted in 2 categories:

**scalars** with the form: "*title*    *type*    *value*"

**arrays** with the form: "*title*    *type*    N=    *length*"

where

*title* is the field name

*type* is the data type (I for integer, R for real, C for characters...)

*value* actual value (for scalars)

*length* number of elements of the vectors or arrays

Vectors or arrays are stored in Fortran order, using 5 columns for floating point numbers (Fortran format, "E16.8"), and 6 column for integers (Fortran format, "I12").

Here, the resources of interest will be:

- the "Cartesian force constants" matrix
- the "Current cartesian coordinates"
- the "Real atomic weights"

## RESOURCES

- Fortran part of the course
- <https://www.gaussian.com/interfacing/>: look at the "FChk File" and "Example FChk File" tabs
- For the quaternion-based rotation:
  - G.R. Kneller, Mol. Sim. 7, 113-119 (1991)
  - G.R. Kneller, J. Chim. Phys. 88, 2709-2715 (1991)

## REQUIREMENTS

The program will have to meet the following requirements:

- The program should support the input of an option file or an interactive mode
- The user should be able to specify two files containing the data of interest. Linux relative paths should be supported. (**optional**) For future extensions, the program should also allow a keyword to specify the type of file (here "fchk" for the formatted checkpoint file)
- The user should be able to control the superposition procedure with the following parameters:
  - first molecule set in Eckart orientation or kept in original orientation
  - superposition of the second molecule using atomic masses or not
  - maximize overlap of full molecule or three atoms chosen by the user.

The default should be that the first molecule is set in Eckart orientation and the second molecule is superposed to it using atomic masses and all atoms.

- The user should be able to specify if the data in output should be the Duschinsky matrix, the shift vector or both.
- For the Duschinsky matrix, the program should check that the matrix is orthogonal and print one of the following piece of information:
  - the full matrix with at least 6 significant digits of precision,
  - the matrix of squared elements of  $\mathbf{J}$ , with at least 6 digits of precision,
  - the highest square element along each row or column, depending on the user choice.
- For the shift vector, the program should print either
  - the shift vector, using a scientific notation, or
  - the maximum displacement in absolute value, the average unsigned displacement and the standard deviation.