EXERCISES FOR MULTIREFERENCE METHODS AND CONICAL INTERSECTIONS

COLUMBUS is a collection of programs for high-level *ab initio* molecular electronic structure calculations. The programs are designed primarily for extended multi-reference (MR) calculations on electronic ground and excited states of atoms and molecules. The COLUMBUS program system is organized as a collection of separate programs (e.g. for calculating the AO integrals, performing SCF, MCSCF or CI calculations, etc.) which communicate via files. In general, each of these programs requires individual input files and generates individual output files. All output files are stored in a subdirectory LISTINGS. The call of the individual programs is handled by scripts. There are two important scripts, the colinp script which is used to generate the inputs for the individual programs and the runc script which is used to run a calculation. More information can be found at the program website: http://www.univie.ac.at/columbus/

Here in order to use the program set the environment
setenv COLUMBUS /u/ac/train19/Columbus5.9

1 Consider the characteristic parameters for different conical intersections:
   a. Ethylene: g=0.113, h=0.071, sx=0.055, sy=0.021
   b. H3: g=0.143, h=0.143, sx=sy=0.00
   c. 5-methyl-2-pyrumidinone: g=0.093, h=0.088, sx=0.101, sy=-0.057

   Characterize the topography of the cone (vertical, tilted, symmetric, etc.) for each case based on these parameters. You can use the equation for the double cone given in the lecture notes and these parameters to generate the energies E1, E2 on a grid around the conical intersection (x,y)=(0,0). If you plot the energies you can create a 3D picture of the conical intersection.

2 Derive the Newton-Raphson equations for locating conical intersections

3 The directory /u/ac/train18/matsika2/h3 contains inputs for the doublet states of the H3 system:
   a. What active space would you use?
   b. Check the input mcdrtin.1 to find the active space used here.
   c. Run $COLUMBUS/mcdrt.x <mcdrtin.1 >&mcdrtls&. Open the output mcdrtls and read the number of configurations created.
   d. Run $COLUMBUS/runc >&h3.log &
   e. Read the number of CSFs used in the MRCI calculation (the size of the MRCI calculation). This number can be found in the h3.log file or in the LISTINGS/cidrtmsls.all file.
   f. Inside the MOLDEN directory there is a molden.freq file which contains the branching vectors. Open this file with MOLDEN. View the two branching vectors as vibrational frequencies. Can you describe/characterize them in terms of the normal modes for H3?

4 The directory /u/ac/train18/matsika2/ethylene contains inputs for ethylene:

a. How many references are in a (2,2) active space? Run $COLUMBUS/mcdrt.x <mcdrtin.1 >&mcdrtls&. Open the output mcdrtls and read the number of configurations created. Did you guess the right number?
b. Run $COLUMBUS/runc >&ethylene.log &
c. Copy the geom.min to geom and rerun the calculation. Do you get the same result?
d. Find the MRCI energies inside the ethylene.log file for the different iterations. Observe how the energies of the two states approach each other.
e. Read the LISTINGS/ciudgls.all file. Search for 'total energy' which is where the final eigenvalues and eigenfunctions of the CI problem are printed. What are the principal configurations for the ground state and the first excited state?
f. Open the file MOLDEN/molden.freq with molden. What is the geometry of ethylene at the conical intersection?