A diagram of a diagram

Description automatically generated with medium confidenceStep by step workflow to do vibronic model diabatization

**0**: Make molecular input (D3h pnictogen hydride or metal trifluoride) using wxMacMolPlt’s builder. Configure directory so it has all necessary scripts and edit *project\_parameters.py* so that the desired normal modes, project folder name, etc. are correct.

**1**: Inside the *gmcpt\_template.inp*, copy and paste the symmetry-correct coordinates into the $data section. Decide whether it is RHF or ROHF MP2 calculation, set multiplicity/charge, and choose basis set. Run this geometry optimization and hessian calculation. You will obtain frequencies, equilibrium geometry, and RHF/ROHF orbitals in the .dat/.out files.

A screenshot of a computer

Description automatically generated**2**: Copy (1)’s input file and turn on the $gmcpt section. Configure the input file such that it is an MCSCF calculation with correct active space. Include the reference geometry and ‘OPTIMIZED RHF/ROHF’ orbitals as $VEC group (orbital eigenvectors) below the $data group. Run this single-point gmcpt calculation. You will receive Semi-canonical MOs. (Note: for metal trifluorides, you may need to look at the orbitals in (2)’s output and ensure that the d-orbitals are HOMO, as sometimes the transition metal’s dz2 orbital is buried below the F orbitals.)

nmofzc=12 nmodoc=12 nmoact=5 nelact=6 mstart(1)=25 icharg = 0 mult = 5 explanation!

Nmofzc (frozen core) = 12 = 1 (Co,1s) + 4 (Co,2s,2p) + 4 (Co 3s,3p) + 3\*(F 1s) = 12

Nmodoc (doubly occupied) = 12 = 3\*(4 from Fluorine: 2s, 2px, 2py, 2pz, 3 electrons transferred from Co, ionic basically)

Nmoact = 5 (active orbitals, the Co’s 5 d-orbs, want to use them for chemistry)

Nelact = 6 (inside the 5 d-orbs, well Co is naturally [Ar]4s3d7, or 9 valence electrons, minus 3 given to 3 Fs, this means that there are 6 electrons active)

Mstart(1) = 25 = nmofzc + nmodoc + 1 = 25, so d-orbs start from here.

The d-orbs and their occupation will look like all spin up, with one beta (spin down) in one d-orb. This makes a multiplicity of 2(S=+2)+1 = 5.

**3**: Copy (2)’s input file and append $DMO group. The $DMO group is determined by your *nmofzc, nmodoc, nmoact* values. For example, if you have 5 active orbitals (nmoact), 1 frozen core orbital (nmofzc), 4 doubly occupied orbitals (nmodoc), then you would give the toolkit script when it asks x y: 5 6. As x = nmoact, y = nmofzc + nmodoc + 1. You are setting the diabatic MOs here and GAMESS will compute reference determinants.

**4**: Copy (3)’s input and append $REFDET group. Run this calculation. Once successful, you can copy this refdet calculation’s input and make it as *temp.inp*. Comment out the $data geometry and add a $data geometry template below $REFDET.

**5**: Run the diabatization program.

***python3 dist\_allmodes\_pm.py gamess\_step1.out***

It will perform linear, bilinear vibronic couplings along a grid of coordinates (according to step size). Once that is all done, rerunning it will produce a mctdh.op file.

**6**: Submit propagation calculations to MCTDH.

The workflow is best explained via video:

NH3 - <https://www.youtube.com/watch?v=Aoo1mgy2H4A&ab_channel=BennyChen>

PH3 - <https://www.youtube.com/watch?v=Aoo1mgy2H4A&ab_channel=BennyChen>