

Time-Dependent Density-Functional Theory (TD-DFT) with DEMON2K: ASESMA Exercises



DEMON stands for *densité de Montréal*. For obvious reasons, the unofficial DEMON logo is a demon or devil, mostly just for fun. This is a picture of Jun Maekawa's devil which is one of the most famous origami devils.

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Chapter 1

Introduction

1.1 Preface

These hands-on lessons have been prepared for the African School on Electronic Structure Methods and Applications (ASESMA) that took place in Accra, Ghana, in June 2025.

ASESMA



The *nominal* objective is

TD, DFT,
MON2K

to learn a bit about how time-dependent (TD) density-functional theory (DFT) works

in a program such as DEMON2K designed for molecules. But the *real* objective is

to learn about static and nondynamical correlation as well as how chemical physicists think about molecules.

Traditionally ASESMA has focused on solid-state physics using periodic quantum physics codes. Quantum chemistry codes for molecules share many of the same principles that underlie periodic codes but with some differences which are partly historical and partly due to an emphasis on solving different types of problems. Let us develop this a little more.

A distinction is sometimes made between chemical physics and physical chemistry. Both are at the interface between chemistry and physics and so it can be hard (and not necessarily even

desirable) to distinguish one from the other. Traditionally chemical physics was done in physics departments and physical chemistry was done in chemistry departments. However a perusal of the table of contents of the American Institute of Physics (AIP) *Journal of Chemical Physics* shows that many chemical physicists are chemistry department faculty. What is going on? I think that the best explanation was given by the Rowlinson [1] who simply pointed out that the mathematics of traditional physical chemistry was adequate for thermodynamics, kinetics, and ion transport, but was relatively elementary compared to the mathematics routinely used in quantum mechanics. Hence, although, quantum mechanics is clearly the best way to model molecules, such work was traditionally relegated to physics departments until sometime in the 1970s. During the 1970s in the USA, quantum mechanics became well-established in physical chemistry courses and theoretical chemical physicists were hired in chemistry departments to do quantum mechanics. We had, in fact, reached the state where there is very little difference between chemical physics and physical chemistry and the identity of these two terms is even recognized in the name of the journal *Physical Chemistry Chemical Physics* (PCCP) published by the Royal Society of Chemistry.

What distinction remains between chemical physics and physical chemistry might best be answered by the somewhat flippant answer of a graduate student to whom I had posed the question of the difference when I was looking for an appropriate school for graduate studies:

“The difference between the two is whether you do the fun part first or save it for last.”

Of course, he did not specify which part is the fun part (and I am sure that varies from person to person!) On a more serious note, chemistry is traditionally centered on chemical reactions. As such it is primarily concerned about how atoms move, with the behavior of electrons in molecules as a secondary concern which can help understand chemical reactivity. In contrast, physicists seem less concerned with chemical reactions and more interested in the properties of molecules which are often determined by what the electrons do when perturbed by (possibly time-dependent) electronic or magnetic fields.

Our purpose in these exercises is to explore strong correlation problems where a single determinantal (SDET) wave function is not enough. Such problems are omnipresent in describing excited states in molecules but are also important for describing ground state potential energy surfaces (PESs) or, as we will often focus on diatomics, potential energy curves (PECs). As a rule, our focus will be on multideterminantal (MDET) wave functions. We will also focus on simple systems—notably H_2 —and use the freely downloadable executable of DEMON2K which can easily be run on any personal computer running LINUX. In this way, we hope that the student will continue to experiment and to learn from DEMON2K, even after this ASESMA meeting.

1.2 Molecular Orbital and Valence-Bond Theory

Let us explore some of the more delicate differences between (solid-state) physics and (quantum) chemistry. These differences are important because they reflect different thought processes motivated both by historical differences and by differences in how mental models are used in these two closely-related fields.

It has frequently been remarked that physics uses plane-wave basis sets while chemistry uses atom centered basis sets. This corresponds to the difference between three types of ideal bonding recognized by chemists. The first type is metallic bonding where the conduction electrons are free to move in the field of ions in a metal. This may be approximated by the homogeneous electron gas (HEG, also known as “jellium”), which is the old particle-in-a-box model with a uniform positive

background to keep the system neutral and including electron correlation. Minimizing the jellium energy leads to a conduction electron density remarkably close to that of sodium metal, making sodium the closest real metal to the HEG.

Long ago, chemists developed an empirical model of two-electron bonding. This was further codified by the use of Lewis dot structures (LDSs) [2]. Note that we will use this term, even when not using dots to represent electrons. Hence $[:N::N:]$, $[:N\equiv N:]$, and $[N\equiv N]$ will all be called LDSs. (We will often put square brackets around our LDSs, though this is not a usual practice in chemistry.) As Lewis noted, this works equally well for describing covalent bonding and ionic bonding because ionic bonds are just extremely polar covalent bonds. LDSs are so deeply ingrained into chemical thinking that it is virtually impossible to work on, say, problems in organic electronics without knowing how to draw the LDSs of the molecules in the study.

LDS

Of course, metallic, covalent, and ionic bonding are just ideal cases. As emphasized, for example, by van Arkel's triangle [3, 4], all real bonds have mixed character. This is further emphasized by applications of the electron localization function (ELF) to lithium clusters [5]. The ELF uses concepts from DFT to reveal electron pairs in molecules. The ELF is localized between atoms for covalent bonds. It also reveals nonbonding lone pair electrons. However lithium clusters, Li_n , are expected to form a covalent bond for the dimer and to gradually show metallic bonding as n increases. In fact, the ELF shows that for many lithium clusters, the electron pairs are actually located in the interstices between groups of atoms, rather than as bonds and lone pairs. This, apparently is what metallic bonding looks like according to ELF.

ELF

The advent of quantum mechanics made it urgent to be able to describe bonding in molecules. Just one year after the publication of Schrödinger's famous paper [6, 7], Heitler and London published a paper which contained the valence-bond (VB) definition of the chemical in H_2 [8]. *This theory is all about spin coupling!* But let us proceed without equations for now. Heitler and London proposed that the wave function for H_2 could be written in two possible ways with one electron of each spin in an s atomic orbital (AO) on each atom, corresponding to the resonance structure $[H\uparrow\downarrow H \leftrightarrow H\downarrow\uparrow H]$. This provided a qualitatively correct description of bonding and greatly pleased chemists who could see the electron pair bond of $[H-H]$. In fact, the resonance structures are identified with $[H-H]$ in VB theory but dissociate into the proper atomic states at long bond distance.

AO

Linus Pauling [9] began his career at the California Institute of Technology with the intention of using quantum mechanics to describe all of chemistry. As he was using VB theory, the wave function of H_2 was

$$\Psi = C_{\uparrow\downarrow}\Psi[H\uparrow\downarrow H] + C_{\downarrow\uparrow}\Psi[H\downarrow\uparrow H], \quad (1.1)$$

so that the energy was (assuming real-valued wave functions),

$$E = \langle \Psi | \hat{H} | \Psi \rangle = |C_{\uparrow\downarrow}|^2 \langle \Psi[H\uparrow\downarrow H] | \hat{H} | \Psi[H\uparrow\downarrow H] \rangle + 2C_{\uparrow\downarrow}C_{\downarrow\uparrow} \langle \Psi[H\uparrow\downarrow H] | \hat{H} | \Psi[H\downarrow\uparrow H] \rangle + |C_{\downarrow\uparrow}|^2 \langle \Psi[H\downarrow\uparrow H] | \hat{H} | \Psi[H\downarrow\uparrow H] \rangle. \quad (1.2)$$

However Pauling and his student George W. Wheland [10, 11, 12] were not only interested in quantitative calculations but also in communicating useful concepts that chemists could use to understand chemical structure and reactivity. In so doing, they took the VB model and described it diagrammatically by using resonance structures. In so doing, they did a slight disservice by simplifying the energy expression to,

$$E = \langle \Psi | \hat{H} | \Psi \rangle \approx |C_{\uparrow\downarrow}|^2 \langle \Psi[H\uparrow\downarrow H] | \hat{H} | \Psi[H\uparrow\downarrow H] \rangle + |C_{\downarrow\uparrow}|^2 \langle \Psi[H\downarrow\uparrow H] | \hat{H} | \Psi[H\downarrow\uparrow H] \rangle, \quad (1.3)$$

in their verbal descriptions. Wheland struggled to make the resonance concept crystal clear:

“the newer concepts can be made clearer with the aid of an analogy. A mule is a hybrid between a horse and a donkey. This does not mean that some mules are horses and the

rest are donkeys, nor does it mean that a given mule is a horse part of the time and a donkey the rest of the time. Instead, it means that a mule is a new kind of animal, neither horse nor donkey, but intermediate between the two and partaking to some extent of the character of each. Similarly, the theories of intermediate stages and of mesomerism picture the benzene molecule as having a *hybrid* structure, not identical with either of the Kekulé structures, but intermediate between them.” — p. 3 of Ref. [10].

Judging from his use of different analogies at different times [12], Wheland was probably not completely happy with any of these explanations. Certainly the “mule = donkey + horse” explanation of resonance in chemistry is wrong because expectation values necessarily contain cross terms.

Molecular orbital (MO) theory was a competing theory for describing the electronic structure of molecules. MOs were typically constructed as linear combinations of atomic orbitals, thereby defining the LCAO approximation. Because MO theory used a SDET of orthonormal MOs, it was much easier for doing calculations than was VB theory which required the use of linear combinations of several SDETs of nonorthonormal AOs. Furthermore, the number of possible resonance structures that needed to be taken into account in VB theory seemed to explode in going to large molecules (i.e., the $N!$ problem of VB theory). For example, VB theory must also include the ionic structures $[\text{H}:\text{H}^+ \leftrightarrow \text{H}^+:\text{H}]$ in the case of H_2 . This is why almost all calculations (including DFT calculations!) are done these days using MO theory.

However VB theory is still very much alive as anyone who has a General Chemistry textbook can attest. While it is true that MO theory is invariably used to describe the electronic structure of diatomics (and the paramagnetism of O_2 is heralded as a victory of MO over VB theory even though Wheland showed how VB theory also predicts paramagnetism [13]), VB hybrid orbitals and bonding concepts are also introduced and resonance structures abound! Moreover, unbeknownst to most chemists, the highly mathematical subject of spin-coupling underlies their VB theory (e.g., [14]) and the only way to explain why benzene resonance structures whose π bonds cross are forbidden is because these structures are actually based upon the Rumer method of spin coupling [15].

World War II is often used as an arbitrary division between classical VB and modern VB theory. With this division the Coulson-Fischer proof of the equivalence of VB and MO configuration interaction (CI) theory falls just barely into the category of modern VB theory [16]. Modern VB theory has overcome many of the old problems of classical VB theory and is now roughly competitive with MO theory [17, 18, 19]. This is not the place to go into modern VB theory. *However VB ideas are extremely useful for the analysis of the dissociation of the ground and excited states of H_2 .*

1.3 Molecular Hydrogen, H_2

The simplest molecule is H_2^+ but the simplest neutral molecule is H_2 for which the potential energy curves are well-known. For example, the following figure is from Ref. [20, 21]:

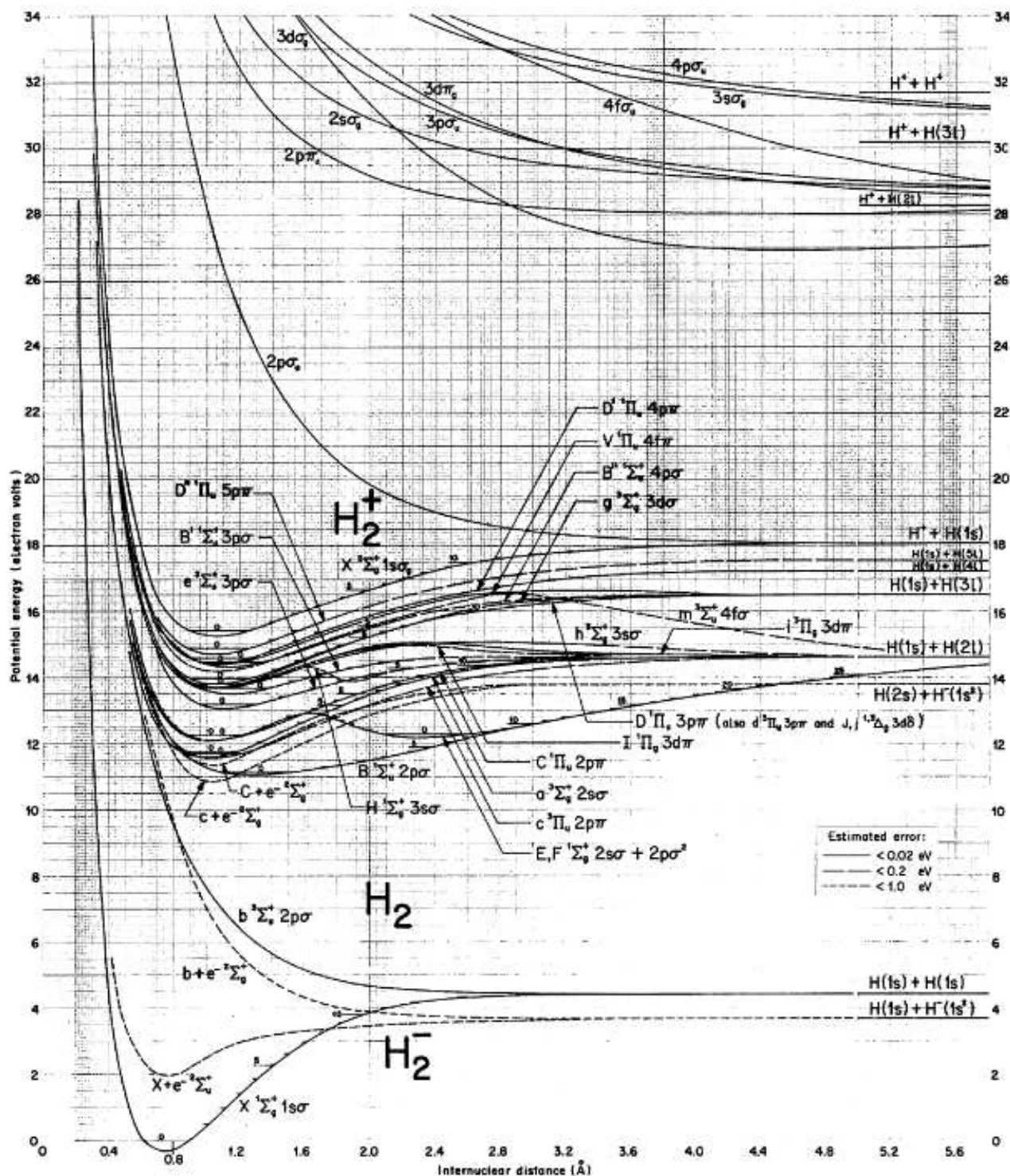


FIG. 2. Potential-Energy Curves for H_2^+ , H_2 , and H_2^-
 A large-scale pullout of this drawing appears at the front of this issue
 In general $1s\sigma$ has been omitted from state designations in order to save space

Note that this graph contains curves not only for H_2 but also curves for H_2^- and for H_2^+ . In general, the more electrons, the lower the energy.

Because of time limitations, we will not try to calculate all of the PECs but will instead focus on the ground state $X^1\Sigma_g$, the first triplet state $a^3\Sigma_u$, and two excited states $B^1\Sigma_u$ and $E, F^1\Sigma_g$. We

will be especially interested in the shapes of the PECs and in how H_2 dissociates for the different states. From the graph, the dissociation of the $X^1\Sigma_g$ and $a^3\Sigma_u$ states is to form $[\text{H}\uparrow\downarrow\text{H} \leftrightarrow \text{H}\downarrow\uparrow\text{H}]$, while the dissociation of the $B^1\Sigma_u$ and $E, F^1\Sigma_g$ states is to form $[\text{H}:\text{H}^+ \leftrightarrow \text{H}^+:\text{H}]$. We will just use the local density approximation (LDA) in its Vosko-Wilk-Nusair (VWN) parameterization [22] and only moderately-sized basis sets.

Chapter 2

Exercises

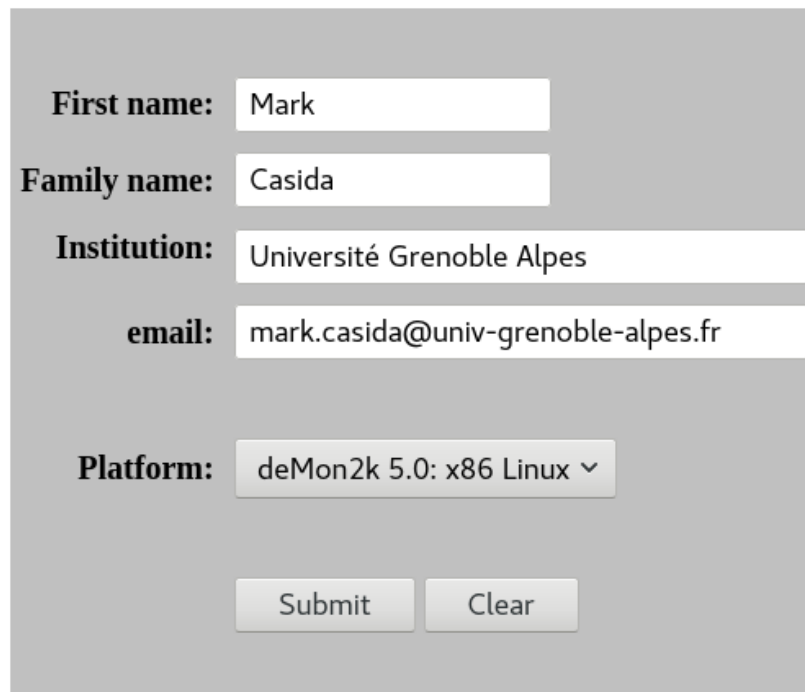
2.1 Installation

This section is taken essentially verbatim from Workbook 1 [23, 24].

DEMON2K should run under most UNIX operating systems. If you do not have a computer running UNIX, it is possible to run UNIX on top of WINDOWS on a PC or on top of the APPLE operating system. An appendix in Workbook 1 explains how Nabila Oozeer installed UNIX on her Mac notebook without removing the APPLE operating system.

Let us assume that you have succeeded in finding or creating a UNIX environment. Let us see how you can install DEMON2K on your machine by looking at how I installed it on my machine. Specifically I installed a binary version on my portable computer which runs CENTOS LINUX. Installation involved several steps:

1. Going to http://www.demon-software.com/public_html/download/binary/download.html?
2. Filling in the form:



First name:	<input type="text" value="Mark"/>
Family name:	<input type="text" value="Casida"/>
Institution:	<input type="text" value="Université Grenoble Alpes"/>
email:	<input type="text" value="mark.casida@univ-grenoble-alpes.fr"/>
Platform:	<input type="text" value="deMon2k 5.0: x86 Linux"/>
<input type="button" value="Submit"/> <input type="button" value="Clear"/>	

3. Creating a suitable directory for unpacking:

```
/home/mcasida/ENGINEERING/workbook/deMon->ls
deMon2k.5.0.x86_linux.tgz
```

4. Changing to that directory and unpacking it:

```
> cd /home/mcasida/ENGINEERING/workbook/deMon
> gunzip deMon2k.5.0.x86_linux.tgz
> ls
deMon2k.5.0.x86_linux.tar
>tar xvf deMon2k.5.0.x86_linux.tar
AUXIS
BASIS
binary
ECPS
FFDS
MCPS
> ls
AUXIS  BASIS  binary  deMon2k.5.0.x86_linux.tar  ECPS  FFDS  MCPS
```

The executable is the file called `binary`. There are also several other files: `BASIS` contains a library of orbital basis sets, `AUXIS` contains a library of auxiliary basis sets for fitting the charge density and exchange correlation (xc) terms, `ECPS` and `MCPS` contain effective core potentials and model core potentials (two very similar concepts) respectively, and `FFDS` contains force field parameters for molecular modeling.

5. Creating a simple input file `deMon.inp` containing:

```
TITLE 02 (Basis: GEN-A3*/6-311++G**)
MULTI 3
#
VXCTYPE VWN
#
PRINT MOS
VISUALIZATION MOLDEEN FULL
#
# --- GEOMETRY ---
#
#
GEOMETRY CARTESIAN ANGSTROM
0      0.000000      0.000000      0.603500
0      0.000000      0.000000     -0.603500
```

This is a single point calculation for the O_2 molecule in its triplet ground state using the LDA.

6. Run the program directly in the directory with the binary:

```
> ./binary < deMon.inp >& deMon.out
> ls
AUXIS  binary                                deMon.inp  deMon.mol  deMon.out  ECPS  MCPS
BASIS  deMon2k.5.0.x86_linux.tar  deMon.mem  deMon.new  deMon.rst  FFDS
> vi deMon.out
```

The program ran correctly, creating several additional files, including the main output in `deMon.out`, a restart file `deMon.rst`, one used for molecular visualization `deMon.mol`, and the files `deMon.meme` and `deMon.new`. The program seems to be working just fine.

2.2 Running the Program

This section is taken verbatim from Workbook 1 [23, 24].

Right now you have a directory (which I will call the `deMon_root` directory) which contains your executable, `BASIS` directory, `AUXIS` directory, etc. For various reasons, you do not want to run in the `deMon_root` directory. Instead, it is convenient to create a `SHELL` program (which I call `run.csh`) to run `DEMON2K` for you and do any clean up you might want to do afterwards. This section provides a simple example of how this is done.

Note that the ending `run.csh` indicates that this program is written in `C SHELL` (`csh`). Other options are possible, but I like `C SHELL`. My program is intended to be small and easily modifiable so that, once you understand it, you can adjust it to your own purposes and start to build your own `SHELL` programs.

My program may be run in any directory of your account. It will look for a `DEMON2K` input file named `xxx.inp` in the same directory where “xxx” can be pretty much anything. Since `DEMON2K` always reads input from a file called `deMon.inp`, the file `xxx.inp` will have to be copied to `deMon.inp`. Also `run.csh` will have to copy the `DEMON2K` executable and any essential directories to the present directory. The job is then run. Once the job has finished, the output file `deMon.out` is renamed `xxx.out` (same “xxx” as for `xxx.inp`) and all the unimportant files are removed. In order to keep things simple, `run.csh` runs `DEMON2K` in foreground.

Here is the contents of `run.csh` which I have placed in the directory `/home/mcasida/ENGINEERING/workbook/examples`.

```
#!/bin/csh
# The previous line indicates that this is a C-shell file
# -----
# Program to run deMon in the present working directory.
# To use: Create an input file with the name xxx.inp where
# xxx can be anything. Execute with
# /home/mcasida/ENGINEERING/workbook/examples/run.csh xxx
# The job runs interactively in foreground.
# -----
set xxx = $1
echo "Input file "$xxx.inp
set PWD = `pwd`
echo "The present working directory is "$PWD
set deMon_root = /home/mcasida/ENGINEERING/workbook/deMon # location of deMon files
echo "Using directories and executables from "$deMon_root
```

```

#
# copy essential files to the present working directory
#
cp $deMon_root/BASIS $PWD # copy the BASIS file to the run directory
cp $deMon_root/AUXIS $PWD # copy the AUXIS file to the run directory
cp $deMon_root/binary $PWD/deMon.x # copy the executable to the run directory
cp $xxx.inp deMon.inp
#
# run deMon
#
./deMon.x
#
# clean up
\rm BASIS
\rm AUXIS
mv deMon.out $xxx.out
\rm deMon.*
# -----
# End of file
# -----

```

Note that comments begin with the “number sign” (#) except for the first line in `run.csh` which tells my computer that this is a `csh` program. The program needs to be made executable:

```
> chmod ugo+x run.csh
```

Let us see how the program works. I have copied the input file from Sec. 2.1 to the directory `/HOME/MCASIDA/ENGINEERING/WORKBOOK/EXAMPLES/LESSON0` as the file `02.inp`. Here is a transcript of my session:

```

> ls
02.inp
> cat 02.inp
TITLE 02 (Basis: GEN-A3*/6-311++G**)
MULTI 3
#
VXCTYPE VWN
#
PRINT MOS
VISUALIZATION MOLDEN FULL
#
# --- GEOMETRY ---
#
#
GEOMETRY CARTESIAN ANGSTROM
0      0.000000      0.000000      0.603500
0      0.000000      0.000000     -0.603500
> /home/mcasida/ENGINEERING/workbook/examples/run.csh 02
Input file 02.inp

```

```
The present working directory is /home/mcasida/ENGINEERING/workbook/examples/Lesson0
Using directories and executables from /home/mcasida/ENGINEERING/workbook/deMon
> ls
02.inp  02.out
```

In addition to the input file 02.inp, I now have my output file 02.out but nothing else. This is enough to get us started.

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