Experiment 7: Integration Grids

The argon dimer, and wiggles that shouldn't be there

Tip

At a glance. 31 Ar_2 distances plus the Ar atom, five functionals, three grids, all with def2-TZVP: **480 jobs**. SG-1 jobs take seconds, SG-2 and SG-3 jobs a few minutes each, so plan your submissions. **You will learn** what the integration grid is, why meta-GGAs are sensitive to it, and how to choose a grid you can trust.

Background

This experiment looks at a subtle issue that can affect the results of any exchange–correlation functional. Kohn–Sham (KS) DFT [1], [2] needs a real-space grid to evaluate the exchange–correlation integrals. Most programs build it with an algorithm Becke introduced in 1988 [3]: the integrals become weighted sums over a finite number of points arranged on spheres around each atom. A grid's "density" is described by its number of **radial** shells and **angular** points per shell; (75,302), for example, means 75 radial shells with 302 points each. The choice of grid can change the results significantly, as Wheeler and Houk showed for the M06 family [4], [5] and Mardirossian and Head-Gordon for two generations of Minnesota functionals [6], [7]. They also point out that meta-GGA functionals usually need finer grids than GGAs.

Choosing the grid is often overlooked, and many practitioners are unaware of the issue. Relying on a program's defaults is not a good idea, even though some programs pick the grid according to the functional [8]. In this experiment you will study the dissociation curve of the argon dimer. The geometries come from the RG10 subset [9] of the MGCDB84 database [10], with the Ar–Ar distance between 3.0 and 6.0 Å. The interaction energy at each distance is

$$\Delta E(r) = E\left(\mathrm{Ar}_2(r)\right) - 2\,E(\mathrm{Ar}).$$

Table 1: Reference interaction energies (kcal/mol) of the argon dimer as a function of the Ar–Ar distance (Å).

r	ΔE	r	ΔE	r	ΔE
3.0	2.24	4.1	−0.23	5.1	−0.07
3.1	1.21	4.2	−0.21	5.2	−0.06
3.2	0.57	4.3	−0.18	5.3	−0.05
3.3	0.18	4.4	−0.16	5.4	−0.05
3.4	−0.06	4.5	−0.14	5.5	−0.04
3.5	−0.19	4.6	−0.13	5.6	−0.04
3.6	−0.26	4.7	−0.11	5.7	−0.03
3.7	−0.28	4.8	−0.10	5.8	−0.03
3.8	−0.28	4.9	−0.09	5.9	−0.03
3.9	−0.27	5.0	−0.08	6.0	−0.02
4.0	−0.25				

Use the functionals B3LYP [11], [12], [13], [14], [15], M06-L [16], M11 [17], M11-L [18] and ωB97M-V [19], [20], and feel free to add others. Use the **def2-TZVP** basis set [21] for all calculations, and try the grids **SG-1**, **SG-2** and **SG-3** (Q-Chem keyword `XC_GRID` = 1, 2 or 3).

Present your results as a dissociation curve like the one in Figure 1, which shows the VSXC functional [22], [23]. Before plotting, collect the data in a table like Table 2.

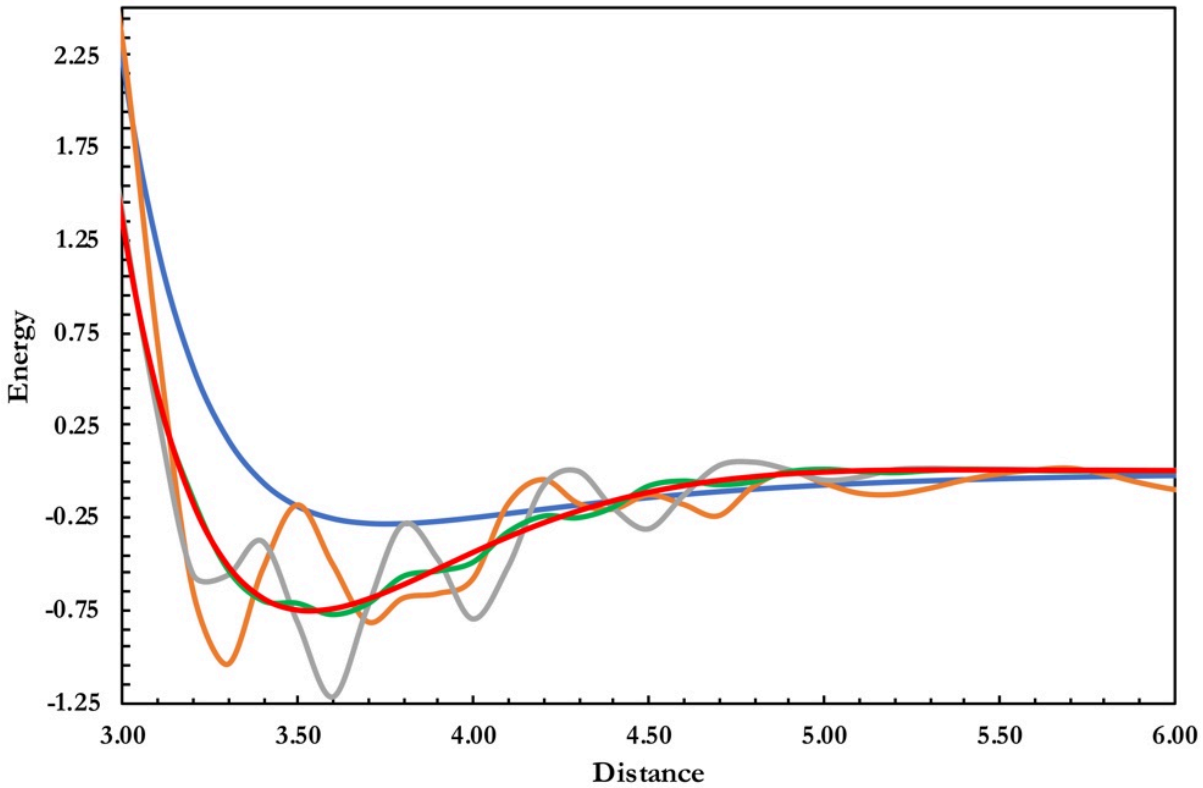


Figure 1: Behavior of the VSXC functional for the Ar dimer with different integration grids: SG-1 (orange), (75,302) (grey), (99,590) (green) and (175,974) (red). The reference curve is blue. Energy in kcal/mol, distance in Å.

Table 2: Data for the SG-1 curve in Figure 1 (VSXC functional; energy in kcal/mol, distance in Å).

r	ΔE	r	ΔE	r	ΔE
3.0	2.33	4.1	−0.18	5.2	−0.12
3.1	0.71	4.2	−0.04	5.3	−0.09
3.2	−0.63	4.3	−0.17	5.4	−0.05
3.3	−1.04	4.4	−0.20	5.5	−0.01
3.4	−0.53	4.5	−0.13	5.6	0.01
3.5	−0.18	4.6	−0.18	5.7	0.02
3.6	−0.50	4.7	−0.24	5.8	−0.01
3.7	−0.81	4.8	−0.08	5.9	−0.06
3.8	−0.69	4.9	0.00	6.0	−0.10
3.9	−0.66	5.0	−0.06		
4.0	−0.58	5.1	−0.12		

Run the calculations

This is the largest set of jobs of the course (5 functionals × 3 grids × 32 structures). SG-1 jobs take seconds, but the finer grids cost much more: expect a few minutes per job with SG-2 and SG-3. Work one functional and one grid at a time, and check the first curve before running the rest. Your instructor may split the functionals across the class.

Collect your results with a script

Reading 480 output files by hand is slow, and it's easy to make mistakes. A small Python script does it for you:

⬇️ **extract_ex07.py**. The same file works on macOS, Windows and Linux.

It reads every Q-Chem output file in a folder, including subfolders. It identifies each job **from what Q-Chem echoed in the output** (functional, `XC_GRID`, basis set and Ar–Ar distance), so your file names don't matter. From each output it takes the total energy, the number of SCF cycles and the wall time, and writes them all to **`ex07_results.csv`** in the same folder. It only *reads* your outputs and never changes them.

Before you start: put all your Experiment 7 output files in one folder. Subfolders, such as one per grid, are fine.

macOS

1. Open **Terminal** (⌘-Space, type *Terminal*, Return).
2. Type `python3 --version` and press Return.
   - If you see `Python 3.8` or newer, you're ready.
   - If a window offers to install the *command line developer tools*, click **Install**, wait a few minutes, then try again.
3. Type `python3` followed by a **space**. Drag `extract_ex07.py` from Finder into the Terminal window, type another space, then drag your **outputs folder** into the window. The line now looks like this:

```
python3 /Users/you/Downloads/extract_ex07.py /Users/you/Documents/Ex7\ outputs
```

4. Press **Return**.

Windows

1. If you don't have Python, install it from python.org/downloads. On the first screen of the installer, tick **"Add python.exe to PATH"**.
2. Open **PowerShell** (Start menu, type *PowerShell*, Enter).
3. Type `py --version` and press Enter. You should see `Python 3.8` or newer. If PowerShell says `py` is not recognized, use `python` instead of `py` in the next step.
4. Type `py` followed by a **space**. Drag `extract_ex07.py` from File Explorer into the window, type another space, then drag your **outputs folder** into the window. The line now looks like this:

```
py C:\Users\you\Downloads\extract_ex07.py "C:\Users\you\Documents\Ex7 outputs"
```

5. Press **Enter**.

Shortcut: if Python came from python.org, you can also **double-click** `extract_ex07.py`. A window opens and asks for the folder. Drag the folder into it and press Enter.

No Python (Colab)

If you can't install Python on your computer, use Google Colab in the browser:

1. Zip your outputs folder (right-click → *Compress* on a Mac, *Send to* → *Compressed (zipped) folder* on Windows).
2. Open colab.research.google.com, create a new notebook, and upload the zip and `extract_ex07.py` with the folder icon on the left.
3. Run this in a cell. Replace `outputs.zip` with your zip's name.

```
!unzip -q outputs.zip -d outputs
!python extract_ex07.py outputs
```

4. Download `outputs/ex07_results.csv` from the file panel (right-click → *Download*).

Read the report: don't skip this step

The script prints a table with the number of usable jobs for each functional and grid. You need **32 in every cell, 480 in total**. Then it lists:

- **Missing jobs**: run them.
- **Problems**: jobs that crashed or hit the 10-minute limit, SCF cycles that didn't converge, a wrong basis set, or a missing `XC_GRID` (Q-Chem's default grid depends on the version and the functional, so it doesn't count as SG-1, SG-2 or SG-3). The script **does not take any energy from these files**. Fix the input, rerun the job, and run the script again.
- **Jobs found more than once**: the script uses the most recent good run. If it says the energies differ, find out why before you trust either one.
- **Not recognized**: other Q-Chem outputs in the folder (for example from another experiment). These are ignored.

You can run the script as often as you like. Each run rereads every output and rewrites the CSV.

⚠️ Use the script carefully

- **Check its work.** Open two or three output files, say one per grid, and compare the total energy, SCF cycles and wall time with the table below (Guide 3 shows where to find them). The script is a tool; the numbers you submit are your responsibility.
- **Don't edit the CSV and save it from Excel.** Depending on your settings, Excel can round the energies or change commas into semicolons. You can *look at* it in Excel, but close it without saving, and import the file exactly as the script wrote it.
- **Keep your output files.** The CSV is a summary, not a replacement for them.

Enter your results

Record the **total energy**, **SCF cycles** and **wall time** of every job. The quickest way is ⬆️ **Import CSV** below: choose `ex07_results.csv` and all three tabs fill in at once. If any cell already holds a different number, the page asks before replacing it. You can also type the values, or paste a column copied from a spreadsheet. The page computes all interaction energies $\Delta E(r) = E(Ar_2) - 2\,E(Ar)$ for you and draws the curves as soon as one is complete.

Explore your data

The dashed black line is the reference curve. Wiggles that the reference doesn't have are grid noise, not chemistry.

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