

Hints on Quantum Chemistry

Quantum Chemistry Codes at MIT

Tips

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Zero of Energy: Most quantum codes compute the "single-point energy" (usually a large negative number) and the "zero-point-energy" (if you asked for second derivatives, force constants, or vibrational frequencies). The zero-point-energy is

$(hc/2)$ sum of vibrational frequencies (omitting any negative frequency). Most partition function formulas assume that the zero of energy is the energy of the ground state of the molecule or TS, i.e.

$E_{\text{single-point}} + E_{\text{zpe}}$ To be consistent,

$K_{\text{eq}} = \exp(-\Delta E/kT) Q_{\text{products}}/Q_{\text{reactants}}$ and $k_{\text{TST}} = (kT/h) \exp(-\Delta E_{\text{TS}}/kT) Q_{\text{TS}}/Q_{\text{reactants}}$.

$\Delta E = E_{\text{single-point}}(\text{Products}) + E_{\text{zpe}}(\text{Products}) - E_{\text{single-point}}(\text{Reactants}) + E_{\text{zpe}}(\text{Reactants})$.

$\Delta E_{\text{TS}} = E_{\text{single-point}}(\text{Transition State}) + E_{\text{zpe}}(\text{Transition State}) - E_{\text{single-point}}(\text{Reactants}) + E_{\text{zpe}}(\text{Reactants})$.

Imaginary or Negative Frequencies: A stable structure should have no negative/imaginary frequencies. A transition state should have one negative/imaginary frequency. If your optimizer converged to a geometry with too many negative/imaginary frequencies, you will need to shift the geometry by hand, and re-run the optimization. Typically this happens with very floppy motions such as internal rotations and sometimes it can be difficult to avoid. If necessary you can constrain the internal rotor coordinate at a gauche or trans conformation, and then optimize the other coordinates. You should look at the normal mode motion which corresponds to imaginary/negative frequencies to see if they correspond to a desired reaction coordinate, or to understand what went wrong with your calculation (and which coordinates need to be adjusted to avoid the problem).

Small systems, easy calculations first! Start from a low level calculation (e.g. semi-empirical) on a simple model of your big system of interest, to get a feel for the geometry you are looking for, and to explore whether there are other local minima you should be aware of. These low-level geometries will help you provide good initial guess geometries for higher level methods.

Normally, one does the final geometry optimization at one level, and a single-point energy at a

higher level of theory (e.g. with a bigger basis set). The second derivative calculation (for the vibrational frequencies) is often done at the same level of theory as the geometry optimization. The notation would be e.g.

MP2 6-31G++*//HF 6-31G*

which means "a single point calculation was done using the 6-31G++* basis and the MP2 correlation correction at a geometry found using the Hartree-Fock method and a 6-31G* basis.

Sometimes an even lower level of theory is used for the second derivative calculation (which can be very expensive). In general, the second derivative calculation should be done at a point where the gradient is zero (at that level of theory), this might be a slightly different geometry than that used for the final geometry optimization and single-point energy calculation.

Internal Rotors: You, the user, must identify any internal rotors in your molecule, and check whether they are hindered enough to be treated as vibrations rather than rotations. Most methyl groups should be treated as internal rotors. To do this, you remove the vibrational frequency that corresponds to the rotor motion from the vibrational partition function, and add an internal rotor partition function. This function can be either that for a free rotor (easy) or that for a hindered rotor (in which case you will need an estimate of the hindering barrier height). Internal rotors have symmetry numbers which contribute to the entropy calculation.

Symmetry numbers: The partition functions are reduced by symmetry numbers; this is because the number of possible quantum states is actually less for molecules of high symmetry than for an nearly identical but less symmetrical molecule. (This is a consequence of the Pauli permutation symmetry requirement on the wavefunction.) The entropy is typically reduced by $R \ln(\text{symmetry number})$. For example, a methyl group internal rotor on an asymmetric backbone has a symmetry number of 3. The NIST group additivity program SP (PC program sold by NIST) attempts to assign symmetry numbers, the numbers it assigns are often but not always correct.

Quantum Chemistry Codes at MIT

There are many different commercial programs for doing quantum calculations. Some compute the thermodynamic quantities for you; for others you can use the programs in the course directory on the MIT server.

- **Gaussian is the most popular quantum chemistry code in the world, and one of the most powerful.**
- **Hyperchem** has an easy graphical user interface, and it runs Molecular Mechanics, Semi-Empirical Calculations, Hartree-Fock, and single-point MP2 calculations.
- **Cerius2** software not recommended for 5.68J/10.652J, but it does have a lot of functionality, particularly for solids, liquids, and macromolecules which is not available in

other packages.

- **Gaussian** can run a wide variety of quantum chemistry calculations, including density functional theory and correlated methods. Gaussian is often run without a graphical interface (though it is a good idea to use the interface, to visually pick up on problems hidden in the numerical output). [Here](#) is a script which can be used to run a Gaussian job through the job queues on matterhorn (this will avoid the possibility of contention between several jobs running at the same time).
- **UniChem** has an easy graphical interface that runs Semi-Empirical and Density-Functional calculations, and it can also set up Gaussian jobs. To save a Gaussian input deck, click Save Deck after you are done with Set Up and Launch. Cut and paste the Gaussian deck out of the .jobG file. Then you can run the Gaussian job through the queues by modifying scriptG, see below. Gaussian can also be run interactively from UniChem, but this is not a good idea for very large jobs.

you can run the following Gaussian script by typing

```
qsub -q regular scriptG
```

You can check its progress with

```
qstat -al
```

and look at

```
/usr2/kinetics/scriptG.out
```

when it is done. The script below can also be found in ~10.652/ QuantumChem/scriptG

```
#!/bin/csh -f  
# below the cat line put your Gaussian job deck
```

```
# You can cut and paste it from a UniChem job deck if desired.  
# WHG has found that with the choice of Mem below  
# the program will run in queue "regular",  
# for larger numbers for Mem you will need  
# to use queue "bigmemory".
```

```
cat >gaussian.deck <<EOF_GAUSSIAN_DECK
```

```
%Mem=25932992
```

```
%nproc=1
```

```
%chk=g92.chk
```

```
#P B3LYP/6-31G(d,p)
```

```
OPT=(GRAD,CARTESIAN,NEWESTMFC)
```

```
OPTCYC=20
```

```
INT(Grid=FineGrid)
```

```
SCF=(DIRECT,TIGHT)
```

```
SCFCYC=64
```

```
test2.10.30.10.35.12
```

```
0 1
```

```
H -0.373088 0.000000 0.000000
```

```
H 0.373088 0.000000 0.000000
```

```
EOF_GAUSSIAN_DECK
```

```
#####
```

```
##### RUN GAUSSIAN
```

```
#####
```

```
/usr2/g94/g94 <gaussian.deck >&/usr2/kinetics/scriptG.out
```

```
# change "/usr2/kinetics/scriptG.out" to your desired output filename
```

```
# please remember to delete your .rwf and .scr files from
```

```
# /usr2/scratch when you are done with your calculation.
```

```
# Be careful not to delete anyone else's .rwf/.scr files
```

```
# if their jobs are running.
```