10. Some practical issues with HF calculations

10.1. Use of Symmetry

The presence of symmetry in a molecule can be used to great advantage in electronic structure calculations.

The most obvious advantage is one step removed from the electronic structure problem, namely geometry optimization. The presence of symmetry elements removes some of the $3N - 6$ degrees of molecular freedom (where $N$ is the number of atoms) that would otherwise be present for an asymmetric molecule. This reduction in the dimensionality of the PES can make the search for stationary points more efficient. For example, benzene ($C_6H_6$), has 12 atoms and the PES formally has 30 dimensions. However, if we restrict ourselves to structures of $D_{6h}$ symmetry, then there are only two degrees of freedom: e.g. the C–C and C–H bond lengths. Finding a minimum on a two-dimensional PES is obviously quite a bit simpler than on a 30-dimensional one.

However, symmetry is also tremendously useful in solving the SCF equations. A key feature is the degree to which it simplifies evaluation of the four-index integrals. In particular, if the functions $\mu$, $\nu$, $\lambda$, and $\sigma$, do not have the right symmetry, then many of the integrals $(\mu\nu|\lambda\sigma)$ will be zero. (This is the same rule as the selection rules that you may remember from the symmetry/group theory classes). The analogous rule holds for the one-electron integrals.

In general the atomic basis functions do not have the symmetry of the molecule, but linear combinations of the various basis functions can be formed that transform according to the symmetry operations of the molecule point group. This process is illustrated below for a HF/STO-3G calculation on water, which belongs to the $C_{2v}$ point group.

The seven atomic basis functions can be linearly transformed to four, two, and one functions belonging to the individual irreducible representations. Because the functions belonging to the different representations do not “mix” (the integral is zero), the matrix breaks down to the block-diagonal form.

The process of solving the HF equations is equivalent to diagonalization of the Fock matrix. Diagonalization of a block diagonal matrix can be accomplished by separate diagonalization of each block. Noting that diagonalization scales as $N^3$, where $N$ is the dimensionality of the matrix, the total time to diagonalize our symmetrized Fock matrix for water compared to the unsymmetrized alternative is:

$$(4^3 + 2^3 + 1^3)/7^3 = 0.21$$

i.e., a saving of almost 80 percent.
Transformation of the minimal water AO basis set to one appropriate for the $C_{2v}$ point group. (from Cramer: Essentials of Computational Chemistry, Theories and Models)

However, there are some hidden dangers in using the molecular symmetry. In particular, if an initial guess for the SCF calculation has a wrong symmetry, since the symmetry adapted basis functions do not interact (the blocks of the Fock matrix are not coupled), the wavefunction is effectively stuck in the symmetry of the starting guess.

As an example, consider the nitroxy radical $\text{H}_2\text{NO}$, which belongs to a $C_s$ point group. The unpaired electron can reside

- in an MO dominated by an oxygen $p$ orbital, which has $a''$ symmetry and gives rise to the $^2A''$ state of the molecule.
- in an MO having $\pi^*_{\text{NO}}$ character that is $a'$ symmetry yielding $^2A'$ state.

When symmetry is imposed, we will have a block diagonal Fock matrix and the unpaired electron will appear in either the $a'$ block or the $a''$ block, depending on the initial guess. Once placed there, most SCF convergence procedures will not provide any means for the electronic state symmetry to change, i.e., if the initial guess is a $^2A'$ wave function, then the calculation will proceed for that state, and if the initial guess is a $^2A''$ wave function, then it will instead be
that state that is optimized. The two states both exist, but one is the ground state and the other an excited state, and one must take care to ensure that one is not working with the undesired state. As shown in the figure below, the \( ^2A' \) is the ground state for short N-O distances, while the \( ^2A'' \) state has lower energy for the longer ones.

10.2 Symmetry in Gaussian

By default, Gaussian will use symmetry in the calculations. The use of symmetry can be completely turned off by keyword \texttt{NoSymm}.

As you already know, \texttt{NoSymm} also suppresses reorienting of the molecule by Gaussian (into the Standard orientation). It can therefore be useful when a particular orientation of the molecule is to be kept.

Further, the use of symmetry can be modified using the \texttt{Symm} keyword, e.g. the point group of lower symmetry can be specified than the actual molecular point group.

10.3 The initial guess

Another useful keyword is \texttt{Guess}, which controls how the initial guess is done. According to the above discussion, when symmetry is used, the initial guess can have a dramatic effect on the outcome of the calculation. We can check and modify the initial guess, using the following options:

\texttt{Guess=Only} \hspace{1cm} This will only plot the initial guess orbital symmetries, but not do any calculation
Guess=Alter  Allows to switch the order of the orbitals in the initial guess. Each such
transposition is on a separate line and has two integers $N_1$ and $N_2$ (free
format, separated by spaces or a comma as usual) indicating that orbital $N_1$
is to be swapped with orbital $N_2$. The list of orbital transpositions is
terminated by the blank line at the end of the input section.

For UHF calculations, two such orbital alteration sections are required, the
first specifying transpositions of $\alpha$ orbitals, and the second specifying
transpositions of $\beta$ orbitals. Both sections are always required. Thus, even
if only $\alpha$ transpositions are needed, the $\beta$ section is required even though it
is empty (and vice-versa). The second blank line to indicate an empty $\beta$
section must be included.

Guess=Mix  Requests that the HOMO and LUMO be mixed so as to destroy $\alpha$-$\beta$
and spatial symmetries. This is useful in producing UHF wavefunctions for
open shell singlet states and should be always included.

For example, consider again the nitrosyl radical. To obtain the initial guess, run this input:

```
%chk=h2no.chk
#UHF/6-31G(d) Guess=Only Stable Test

nitrosyl radical

  0 2
  N  -0.044  0.000  -0.729
  O   0.009  0.000   0.795
  H   0.229  0.825  -1.244
  H   0.229 -0.825  -1.244

This is the output:

Initial guess orbital symmetries:
Alpha Orbitals:
  Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A')
  Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A')
    ....
Beta  Orbitals:
  Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A')
  Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A')
    ....
The electronic state of the initial guess is 2-A'.

We have an unpaired electron in the A' orbital, and the initial guess electronic state is doublet
A'. That corresponds to the ground state for short N-O distances, as expected.

If we run this job at UHF/6-31G(d) level, we obtain:
SCF Done:  E(UHF) = -130.343490309  A.U. after 23 cycles
Convg  =  0.6928D-08  -V/T =  2.0058
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000 <S**2>= 0.7738 S= 0.5118

This is a pretty good value of spin (we expect $S^2 = 0.75$  $S=0.5$) and the orbital symmetries are:

Alpha Orbitals:

- Occupied  (A') (A') (A') (A') (A') (A') (A') (A')
- Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')

Beta Orbitals:

- Occupied  (A') (A') (A') (A') (A') (A') (A') (A')
- Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A')

The electronic state is 2-A'.

The electronic state stays doublet A'.

Now let’s say we want to try what happens if we start with the other state - the 2-A". To force the initial guess into that symmetry, we will flip the HOMO A' (which is number 9), with the nearest virtual orbital with A" symmetry (number 12), for the $\alpha$ spin orbitals.

Remember that Guess=Alter requires the permutation numbers for both alpha and beta orbitals, separated by a blank line. If there is nothing for the beta orbitals, then we need two blank lines.

%chk=h2no.chk
#UHF/6-31G(d) Guess=Alter Test

Nitrosyl radical A"

0 2
N -0.044  0.000 -0.729
O  0.009  0.000  0.795
H  0.229  0.825 -1.244
H  0.229 -0.825 -1.244

9 12

This is what we get:

... Pairs of Alpha orbitals switched: 9 12
No Beta orbitals switched.

Initial guess orbital symmetries:
Alpha Orbitals:
Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A'') (A') (A'') (A'')
Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A'') ...

Beta Orbitals:
Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A'') (A''')
Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A') (A'') (A''') (A'')

The initial guess is switched and the ground state is \(^2\text{A}''\). The UHF calculation in this case also converges to the \(^2\text{A}''\) state:

\[
\text{SCF Done: E(UHF) = -130.343490309 A.U. after 24 cycles} \\
\text{Convg = 0.2157D-08} \\
\text{-V/T = 2.0058} \\
\text{<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000 <S**2>= 0.7738 S= 0.5118} \\
\]

Alpha Orbitals:

\[
\text{Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A'') (A') (A'') (A'')} \\
\text{Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A'')} \\
\]

Beta Orbitals:

\[
\text{Occupied  (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A'')} \\
\text{Virtual   (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A') (A'')} \\
\]

The electronic state is \(^2\text{A}'\).

Obviously, the SCF converged to the right ground state \(^2\text{A}'\). We did not manage to fool it this time: the default algorithm is pretty robust.

### 10.4. Initial guess in optimizations and PES scans

When you run optimizations or potential energy scans, and you need to alter or mix the guess at each step, use, respectively, `Guess=(Alter,Always)` and `Guess=(Mix,Always)`.

The `Always` option forces the program to generate a new initial guess at each step of the optimization instead of reading it from the converged calculation at the previous step. This way you can start afresh and modify your guess at will independently of what the calculation at the previous point converges to.

Remember that `Guess=(Mix,Always)` must be used for scans of open-shell singlets.

### 10.5. Forcing SCF to converge to a given state

Now suppose we really want to keep the molecule in the \(^2\text{A}''\) state. For example, we want to scan the energy as a function of the N-O distance as in the above figure. That can be done

- by the proper initial guess and
- specifying an algorithm for SCF that will be less likely to break the symmetry constraint: `SCF=QC`. (The “QC” stand for quadratically convergent).
Running this input:

%chk=h2no.chk
#UHF/6-31G(d) SCF=QC Guess=Alter Test

Nitrosyl radical A''

0 2
N -0.044 0.000 -0.729
O 0.009 0.000 0.795
H 0.229 0.825 -1.244
H 0.229 -0.825 -1.244

9 12

we get:

SCF Done: E(UHF) = -130.024666834 a.u. after 24 cycles
Convg = 0.1926D-07 105 Fock formations.
S**2 = 1.7810 -V/T = 2.0003
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000 <S**2>=1.7810 S=0.9251

The electronic state is 2-A''.

The energy is higher, the spin contamination a bit alarming, but it did force the molecule to stay in the 2-A'' state.

We could in principle scan the potential energy surfaces, or at least pieces of them, as pictured above. However, it is difficult to do automatically, using relaxed (or rigid) surface scan, because at each step we would have to:

- determine what the initial guess is (it does change with the molecular geometry)
- alter the initial guess correspondingly
- make sure the SCF converged to the desired electronic state.

10.6. SCF Stability

A stability calculation determines whether there is a lower energy wavefunction corresponding to a different solution of the SCF equations.

If a stability calculation indicates an unstable wavefunction for a system for which you were attempting to model its ground state, then the calculation does not in fact correspond to the ground state, and any energy comparisons for or other conclusions about the ground state based on it will be invalid.

The following Gaussian keywords will be of use:

Stable

Tests the stability of the SCF solution computed for the molecule. This involves determining whether any lower energy wavefunction exists for the system, obtained by relaxing constraints placed on it by default (e.g., allowing the wavefunction to become open shell or reducing the symmetry of the orbitals).
Stable=Opt  Test the stability of the SCF solution and reoptimize the wavefunction to the lower energy solution if any instability is found. Optimizing the wavefunction, we are not referring to a geometry optimization, which locates the lowest energy conformation near a specified starting molecular structure. Predicting an SCF energy involves finding the lowest energy solution to the SCF equations. Stability calculations ensure that this optimized electronic wavefunction is a minimum in wavefunction space and not a saddle point—which is an entirely separate process from locating minima or saddle points on a nuclear potential energy surface.

Let us test the nitrosyl wavefunction for stability, i.e. include Stable in the route section.

This is the we found in the output file:

The wavefunction is stable under the perturbations considered.

If we alter the initial guess and use SCF=QC to force the nitrosyl radical to the $^2A''$ state, the stability test yields to following:

The wavefunction has an internal instability.

The stability test indicates, as we already know, that the solution is not stable, i.e. the SCF did not converge to the true minimum. To fix that, specify Stable=Opt.

This will first tell you again that there is an instability:

The wavefunction has an internal instability.

But later, after the optimization is done:

The wavefunction is stable under the perturbations considered.
The wavefunction is already stable.

It found the true minimum - the $^2A'$ solution with the right energy and spin:

SCF Done:  E(UHF) = -130.343490310     a.u. after 38 cycles
          Convg = 0.1153D-06                  182 Fock formations.
          S**2 = 0.7738                      -V/T = 2.0058
...
The electronic state is $2-A'$. 