

9. Open shell systems

The derivation of Hartree-Fock equations (Chapter 7) was done for a special case of a *closed shell* systems. Closed shell means that each MO is occupied by two electrons with the opposite spin. The total spin of the system, which is the (vector) sum of all electron spins, is zero:

$$\hat{S} = \sum_{i=1}^N s_i(i) = 0 \quad (61)$$

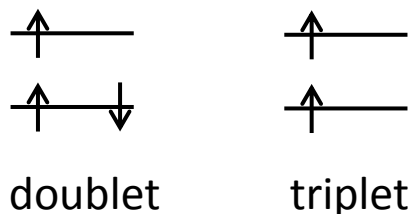
This is called a *singlet* or *spin singlet*, because the so called *multiplicity*, or number of possible orientations of the total spin, which is

$$\text{multiplicity} = 2S + 1 \quad (62)$$

is one for $S = 0$.

The S is the spin quantum number and can take half integer and integer values, i.e. $S=0, 1/2, 1, 3/2, 2$ etc. The quantum numbers S come from the allowed values of the total spin operator \hat{S}^2 which are $S(S+1)$ in the units of \hbar (but in atomic units this is 1). Therefore, we say that the square of the total spin is $S(S+1)$, where S is the quantum number (not S^2)

By contrast, *open shell* systems are those where all electrons are not paired. For example, a radical or atom with a single unpaired electron is a doublet, because $S=1/2$ and $2S+1=2$. An atom or a molecule with two electrons with the same spin is a triplet, because $S=1$, therefore $2S+1=3$.

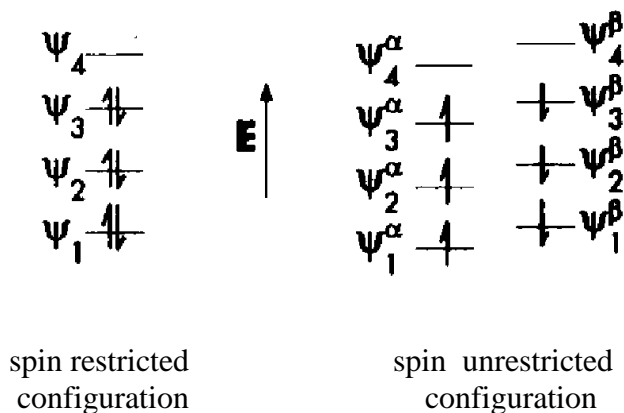


We have:

spin quantum number S	multiplicity $2S+1$	total spin $S^2 = S(S+1)$
0	1 (singlet)	0
1/2	2 (doublet)	0.75
1	3 (triplet)	2
3/2	4 (quartet)	3.75
2	5 (quintet)	6

9.1. Restricted and unrestricted configurations.

There are two ways to describe the electron configurations in open shell systems: *restricted* and *unrestricted*:



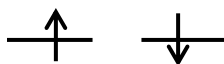
- *Restricted configurations*, restrict both spins α and β to have the same spatial orbitals.
- *Unrestricted configurations* allow each spin (α or β) to have a different spatial orbital.

Each description has some advantages as well as drawbacks:

Restricted configurations:

- Restricted open shell wavefunctions have correct and well defined value of the total spin (e.g. $S=0, 1/2, 1$ etc. which translates to singlet, doublet, triplet etc.). In the language of quantum mechanics, they are eigenfunctions of the total spin operator \hat{S}^2 .
- However, in some cases the wavefunction with the proper spin and antisymmetry *cannot* be described as a *single Slater determinant*!

Consider, for example, an open shell singlet, such as singlet state of the oxygen molecule $^1\text{O}_2$:



The proper singlet wavefunction is:

$$\Psi(1, 2) = \frac{1}{2} [\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (63)$$

you can try for yourself that this function cannot be written as a single determinant, but as a combination of two:

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} \det \begin{pmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_2(2)\beta(2) \end{pmatrix} + \frac{1}{\sqrt{2}} \det \begin{pmatrix} \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) \\ \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) \end{pmatrix} \right] \quad (64)$$

- They do not take into account *spin polarization*. This arises because electrons with the same spin interact differently than those with different spin.

Unrestricted configurations:

- Unrestricted wavefunctions allow different spatial distribution for electrons with α spins and β spins and therefore can describe *spin polarization*. Spin polarization occurs due to exchange-correlations effects via the interactions of the electrons of the same spin as an unpaired electron in the open shell (e.g. radical) system.
- Unfortunately, unrestricted wavefunctions do not have the proper and well defined value of spin, i.e. are not eigenfunctions of \hat{S}^2 . They suffer from the *spin contamination* by states with higher spin. For example, singlet states will be contaminated (have an admixture) of triplet, quintet etc. states, while doublets will be contaminated by quartets, sextets etc.

9.2. Restricted Open Shell Hartree-Fock (ROHF) theory.

Extension of HF equations to the restricted open shells is called, go figure, restricted open shell Hartree-Fock (ROHF). The ROHF Roothan-Hall equations would be formally the same as those for the closed shell system, except the density matrix elements for the singly occupied orbital(s) are not multiplied by the factor of two.

Because they neglect spin polarization and require multi-determinant wavefunctions, they are seldom used for the open shell calculations (there is a more powerful multi-determinant method, called multi-configurational self-consistent field MCSCF, we will talk about later).

9.3. Unrestricted Hartree-Fock (UHF) theory: Pople-Nesbet equations

Unrestricted HF theory (UHF) is almost exclusively used for the open shell problems.

To permit the α and β spins to occupy different regions of space, it is necessary to treat them individually in the construction of the molecular orbitals. For this case, the α and β electrons are in different orbitals, resulting in two sets of molecular orbital expansion coefficients:

$$\begin{aligned} \psi_i^\alpha &= \sum_{\mu=1}^M C_{i\mu}^\alpha \phi_\mu^{AO} \\ \psi_i^\beta &= \sum_{\mu=1}^M C_{i\mu}^\beta \phi_\mu^{AO} \end{aligned} \quad \text{for } i = 1, 2, \dots, N/2 \quad (58)$$

The two sets of coefficients result in two sets of Fock matrices (and their associated density matrices), and ultimately to a solution producing two sets of orbitals. These separate orbitals

produce proper dissociation to separate atoms, correct delocalized orbitals for resonant systems, and other attributes characteristic of open shell systems.

The individual orbitals are found by carrying out separate HF calculations for each spin, with the spin-specific Fock operator now defined as:

$$\begin{aligned} F_{\mu\nu}^{\alpha} &= H_{\mu\nu}^{core} + \sum_{\lambda\sigma} \left[P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta} \right] (\mu\nu|\lambda) - P_{\lambda\sigma}^{\alpha} (\mu\lambda|\sigma\nu) \\ F_{\mu\nu}^{\beta} &= H_{\mu\nu}^{core} + \sum_{\lambda\sigma} \left[P_{\lambda\sigma}^{\alpha} + P_{\lambda\sigma}^{\beta} \right] (\mu\nu|\lambda) - P_{\lambda\sigma}^{\beta} (\mu\lambda|\sigma\nu) \end{aligned} \quad (59)$$

resulting in unrestricted equivalents of Rooth-Hall equations, called Pople-Nesbet equations:

$$\begin{aligned} \mathbf{F}^{\alpha} \mathbf{C}^{\alpha} &= \varepsilon^{\alpha} \mathbf{S} \mathbf{C}^{\alpha} \\ \mathbf{F}^{\beta} \mathbf{C}^{\beta} &= \varepsilon^{\beta} \mathbf{S} \mathbf{C}^{\beta} \end{aligned} \quad (60)$$

9.4. Spin contamination

Remember that the eigenfunctions are NOT pure spin states, but contain some amount of spin contamination from higher states (for example, doublets are contaminated to some degree by functions corresponding to quartets and higher states).

For example, an unrestricted calculation on a CH radical:

```
#UHF/6-31G Test

C-H radical

0 2
C
H 1 1.05
```

should be a doublet (spin multiplicity 2). The total spin S^2 should be 0.75. This is what we read in the output:

```
SCF Done: E(UHF) = -38.2484620416 A.U. after 11 cycles
          Conv = 0.7086D-08 -V/T = 1.9964
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000 <S**2>= 0.7529 S= 0.5015
<L.S>= 0.000000000000E+00
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7529, after 0.7500
```

The S^2 after the UHF calculation was 0.7529 - a little higher than 0.75. It was therefore contaminated by a higher spin, although not too much. Gaussian tries to correct for the contamination, by so-called annihilation method. In this case the contribution of the higher spin component was annihilated completely, giving the right spin of 0.75.

9.5. Unrestricted calculations in Gaussian

Unrestricted calculations are called with the prefix `U` before your method in the Route section of the input. For example, an unrestricted HF/STO-3G calculation would be

```
#UHF/STO-3G Test
```

The unrestricted, open-shell calculations can be a lot trickier than the closed shell restricted cases. You should always examine the results carefully and use intuition, check spin contamination, and take advantage of `Stability` tests (see below) to make sure your solution is the correct one.

Notes:

- Unrestricted calculations can do everything restricted ones can do (optimizations, frequencies, scans, orbitals etc.).
- If you have an unpaired electron or electrons (i.e. doublet, quartet etc.), Gaussian will automatically run an unrestricted calculation.
- If you call an unrestricted calculation on a closed shell system, it will converge to a restricted solution: there is an equal number of both spins so there is no reason for the spatial orbitals to be different for each of them.
- For open shell singlets it is necessary to use `Guess=Mix` keyword to force the calculation to be truly unrestricted. This ensures that the HOMO and LUMO are mixed so as to destroy both α - β and spatial symmetries.
- For optimizations or PES scans on open-shell singlets, use `Guess=(Mix,Always)`. This will ensure that the new initial guess is done at every step of the optimization or PES scan. More about initial guesses after additional practical issues (namely the symmetry) are discussed.

10. A few practical issues with HF calculations

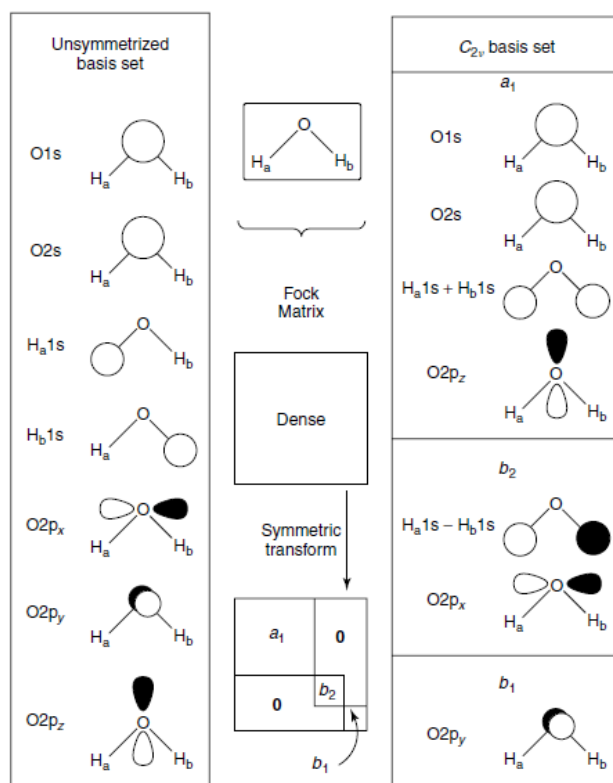
10.1. Use of Symmetry

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 removes some of the $3N - 6$ degrees of molecular freedom (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 can be also tremendously useful for 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 μ , ν , λ , and σ , 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:



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*)

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:

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

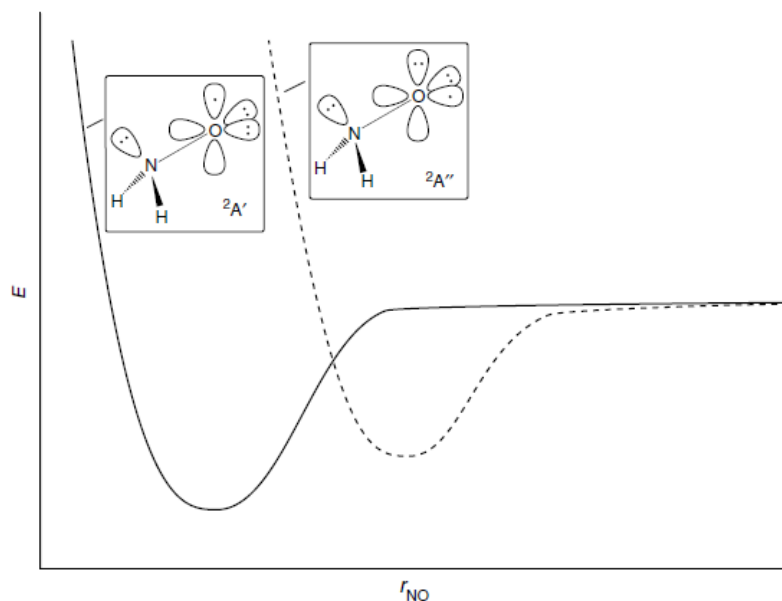
i.e., a saving of almost 80 percent.

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 nitroxyl radical H_2NO , which belongs to a Cs 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 π^*_{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 `NoSymm`.

As you already know, `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 `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 `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:

<code>Guess=Only</code>	This will only plot the initial guess orbital symmetries, but not do any calculation
<code>Guess=Alter</code>	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 α orbitals, and the second specifying transpositions of β orbitals. Both sections are always required. Thus, even if only α transpositions are needed, the β section is required even though it is empty (and vice-versa). The second blank line to indicate an empty β section <i>must be included</i> .
<code>Guess=Mix</code>	Requests that the HOMO and LUMO be mixed so as to destroy α - β 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'') (A')
....
Beta  Orbitals:
  Occupied  (A') (A') (A') (A') (A'') (A') (A') (A'')
  Virtual   (A') (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. Running 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:
  Alpha Orbitals:
  Occupied (A') (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'')
```

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 $^2A''$. 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 α 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'')

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'')

...

The initial guess is switched and the ground state is $^2A'$. The UHF calculation in this case also converges to the $^2A'$ state:

```
SCF Done: E(UHF) = -130.343490309 A.U. after 24 cycles
           Conv = 0.2157D-08 -V/T = 2.0058
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000 <S**2>= 0.7738 S= 0.5118
```

...

Alpha Orbitals:

Alpha Orbitals:

Occupied (A') (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'')

The electronic state is $2-A'$.

...

Obviously, the SCF converged to the right ground state $^2A'$.

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 $^2A''$ 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 the following 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
```

yields:

```
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 $^2A''$ 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'.
```