Cent. Eur. J. Chem. • 9(4) • 2011 • 567-571
DOI: 10.2478/s11532-011-0047-1

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Central European Journal of **Chemistry**

An analysis of SCF and geometry convergence for diatomic molecules

Invited Paper

Cory C. Pye

Department of Chemistry, Saint Mary's University,
Halifax, NS Canada B3H 3C3

Received 13 January 2011; Accepted 11 April 2011

Abstract: A geometry and SCF convergence study of Hartree-Fock calculations using the 6-31G* basis set is carried out on the set of all possible diatomic molecules formed from atoms with $Z \leq 36$. The utility of Hartree-Fock calculations using the smaller STO-3G basis set to improve the convergence behavior is demonstrated.

Keywords: *Self consistent field • Geometry optimization • Convergence • Guess*

1. Introduction

The advent of modern computers has led to a proliferation of computational chemistry to such an extent that it is no longer the domain of the specialist. Computational chemical programs, supported by graphical user interfaces, have become much easier to use. However, the ease by which properties such as energy and geometry are obtained can sometimes be hampered by convergence difficulties. To remedy these problems, convergence acceleration schemes are sometimes used such as Pulay's direct inversion in the iterative subspace (DIIS) for wavefunction [1] and geometry [2] convergence. Another way to improve the convergence is to use a good initial guess for either the wavefunction or the geometry. In this paper, the use of HF/STO-3G [3] geometry and wavefunction guesses for HF/6-31G* [4] calculations is explored.

2. Computational Details

Gaussian 98 [5] was chosen as the computational program. Input files for all 666 possible diatomic (neutral) molecules that could form betweem a pair of atoms selected from H-Kr were prepared. This set was chosen as both the STO-3G and 6-31G* basis sets are available for these atoms. The multiplicity was set to either 1 or 2, depending on whether the number of electrons was even or odd. The starting geometry was chosen as 200 pm (2.0 Å). Default geometry optimization and self-consistent field (SCF) convergence criteria were used unless otherwise specified, except that z-matrix input and optimization coordinates were used.

3. Results and Discussion

3.1 Assessment of default HF/6-31G* calculations

Fig. 1 presents the results of the standard HF/6-31G* calculations. The majority of the calculations finished without any problems. The most common error (Set 1: 96 cases, 14.4%) was that the SCF failed to converge on the first step. A definite trend is noted in that the vast majority of these systems contained at least one transition metal, and that the majority had spin multiplicity of 2 which defaults to an unrestricted Hartree-Fock (UHF) calculation. The second-most common error (Set 2: 24 cases, 3.6%) is that the SCF failed to converge after a few geometry convergence cycles. The majority of these also had spin multiplicity of 2 (UHF wavefunction). The third most common error (Set 3: 18 cases, 2.7%) is failure of the optimizer (taking a bad step). For these, the Hessian matrix becomes negative. The majority of these occur where both atoms have Z<10, whose optimized

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* *E-mail: cory.pye@smu.ca*

distances are presumably much less than the default 200 pm chosen. The geometry decreases significantly for these before failure. For the others, the geometry keeps increasing until the Hessian becomes negative. The fourth most-common error (Set 4: 9 cases, 1.4%) is failure of the geometry optimizer to converge at all. In these cases, the distance between the atoms simply keeps increasing until the maximum number of steps (20) is exceeded. This only occurs for some diatomic molecules in which both of the atoms are a group 1, 2, 12, or 18 element. The forces are typically converged, but the predicted step size is large.

3.2 HF/6-31G* calculations using an HF/STO-3G wavefunction guess

The most common failure mode of the test set was failure of the SCF to converge at the first step. Using a converged HF/STO-3G wavefunction as an initial guess for the HF/6-31G* calculation might be expected to improve the success rate of convergence. It would not be expected to improve the geometry convergence problems. Fig. 2 presents the results of the HF/6-31G* calculations attempting to use a converged HF/STO-3G wavefunction on the 97 Set 1 molecules. The most common result (49, 51.0% of Set 1) was that both the HF/STO-3G and HF/6-31G* calculation now converged. The second most common result (29, 30.2%) was that the HF/STO-3G calculation converged, but the HF/6-31G* SCF failed on the first step. The third most common result (11, 11.5%) was that the HF/STO-3G calculation also failed to converge. The fourth most common result (5, 5.2%) was that the HF/STO-3G calculation converged, but the HF/6-31G* SCF failed at some later stage of the optimization. The least common result (2, 2.1%) was that the HF/STO-3G calculation converged, but the HF/6-31G* geometry optimization failed. Clearly, use of the HF/STO-3G wavefunction leads to improved success in the problem SCF cases identified earlier (Set 1).

3.3 HF/6-31G* calculations using an HF/STO-3G geometry guess

The second most common failure mode of the test set was failure of the geometry to converge. Using a converged HF/STO-3G geometry as an initial geometry guess for the HF/6-31G* calculation might be expected to improve the success rate of geometry convergence. It might also assist with the SCF convergence of problem cases if the optimized HF/STO-3G and HF/6-31G* geometries are similar. Fig. 3 presents the results of the HF/6-31G* calculations attempting to use a converged HF/STO-3G geometry on the 150 Set 1-4 molecules. Surprisingly, the most common result (46, 30.7%) is that the HF/STO-3G SCF fails to converge. The reason that this number is higher than above (Section 3.2, 11 cases) is that the default SCF convergence criteria are more stringent for geometry optimizations than for SCF calculations, and so many cases which converged with loose criteria do not converge with the more stringent criteria. The second most common result (40, 26.7%) is that both the HF/STO-3G and HF/6-31G* parts converge. For Set 4 molecules, we note that with one exception, using the HF/STO-3G geometry as an initial guess converges the HF/6-31G* geometries. We note the convergence of 3 additional Set 3 molecules, 5 additional Set 2 molecules, and 19 additional Set 1 molecules. The convergence of these last two sets shows that using even just a HF/STO-3G geometry can result in HF/6-31G* SCF improvements. The third most common result (27, 18.0%) is that the HF/STO-3G calculation converges, but the HF/6-31G* calculation fails on the first step. The fourth most common result (15, 10.0%) is that the HF/STO-3G SCF fails to converge at some later geometry step. The fifth most common result (14, 9.3%) is that the optimization at HF/STO-3G takes a bad step (mostly for diatomics whose atoms have $Z<10$). A smattering of other situations arise in which the HF/STO-3G geometry and SCF converges, but the HF/6-31G* SCF fails at a later step (4, 2.7%) or the geometry fails to converge (3, 2.0%); or even the STO-3G geometry doesn't converge (1, 0.7%).

3.4 HF/6-31G* calculations using an HF/STO-3G geometry and wavefunction guess

It might be supposed that using both a HF/STO-3G geometry and wavefunction guess should lead to improvements in both the HF/6-31G* SCF and geometry optimization. In addition, because of the improvement in the HF/6-31G* SCF convergence by use of an optimized HF/STO-3G geometry in some cases, there may be some additional synergies in the SCF convergence. However, we must avoid failure to converge the HF/STO-3G SCF because of the more stringent criteria required for optimization. This can be done by using single-point convergence criteria during the optimization. While this might result in the HF/STO-3G geometries not quite being converged had the more stringent criteria been used (i.e. somewhat greater noise), the uncertainty in the geometry is probably smaller than the difference between the optimized HF/STO-3G and HF/6-31G* geometries and might be an attractive strategy. We present these results in Fig. 4. Of the 150 calculations on Sets 1-4, the most common result (62, 41.3%) is that both the HF/STO-3G

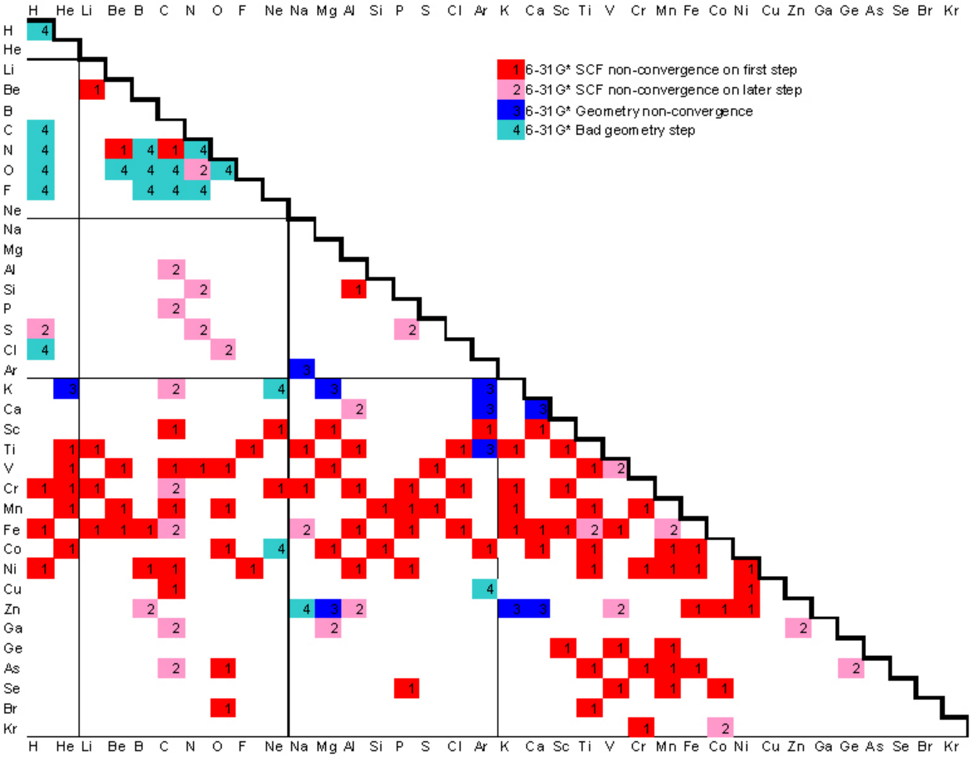

Figure 1. Results of running HF/6-31G* optimization calculations on the test set. The position in the figure identifies the particular diatomic. White indicates normal completion. Red values indicate that the SCF failed to converge on the first step. Pink values indicate that the SCF failed to converge at some later geometry step. Blue values indicate that the geometry did not converge. Green values indicate that the geometry took a bad step which resulted in an optimization error.

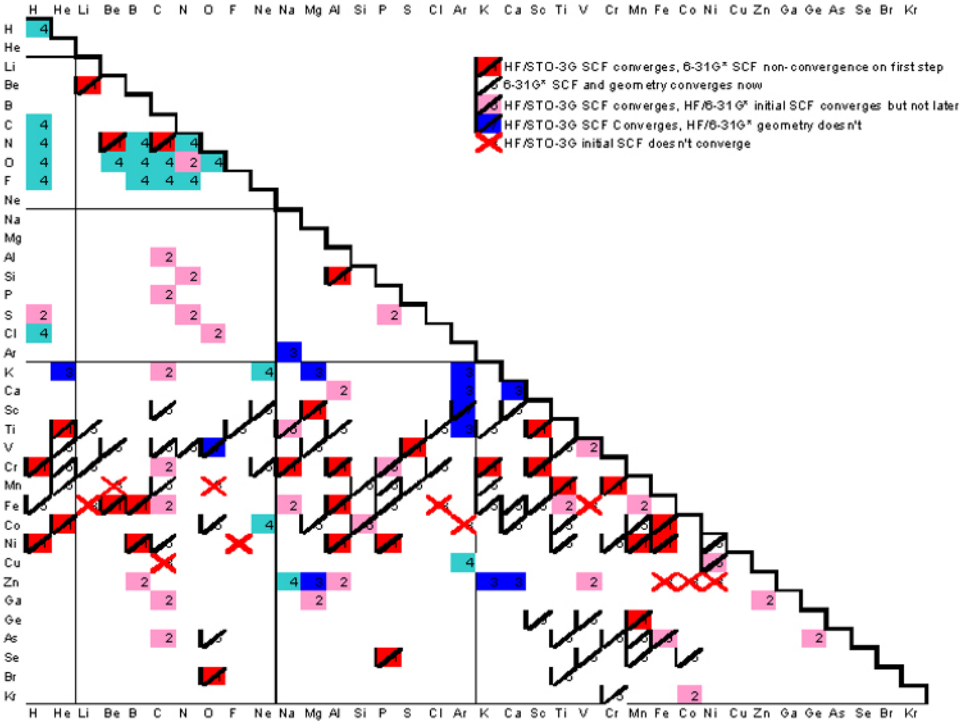

Figure 2. Results of running HF/6-31G* optimization calculations on the Set 1 molecules. A black checkmark indicates the HF/STO-3G SCF calculation was successful. A red X indicates the HF/STO-3G calculation failed to converge.

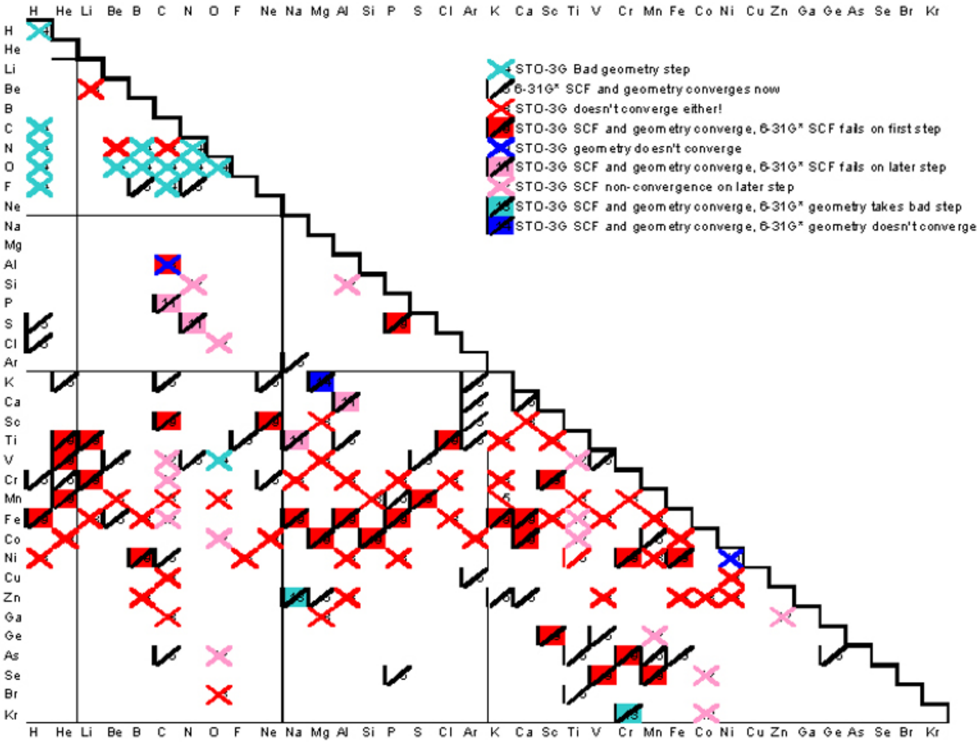

Figure 3. Results of running HF/STO-3G optimization, followed by HF/6-31G* optimization calculations on the Set 1-4 molecules starting with the STO-3G geometry (but not the wavefunction). A black checkmark indicates the HF/STO-3G geometry calculation was successful. A red X indicates the HF/STO-3G SCF calculation failed to converge on first step, a pink X indicates that the HF/STO-3G calculation failed at a later step, a blue X indicates that the HF/STO-3G geometry failed to converge.

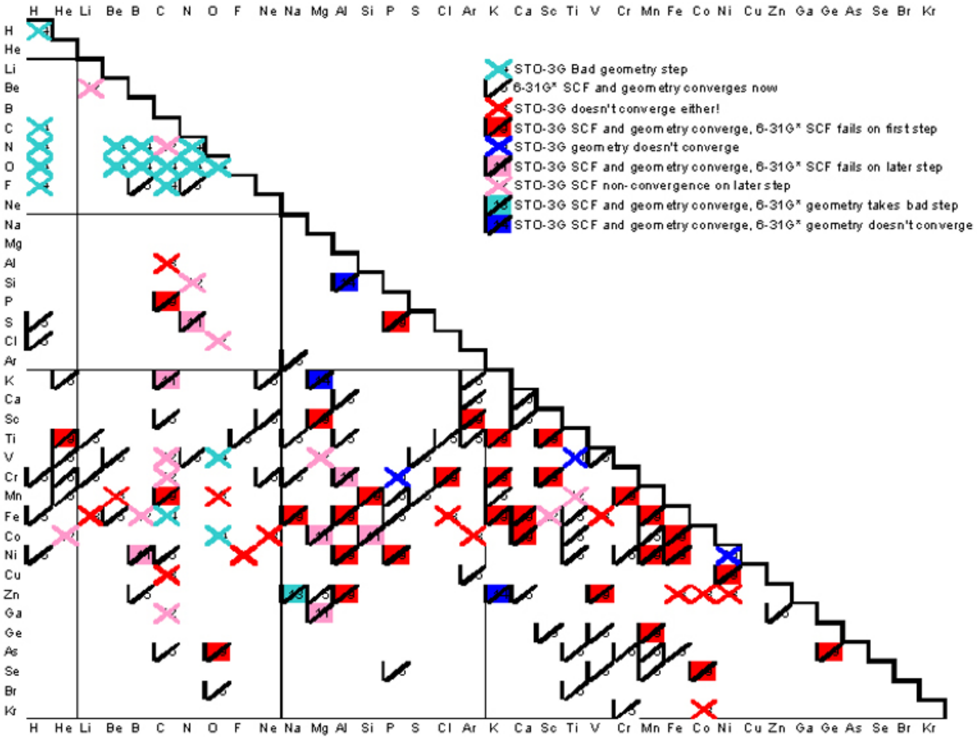

Figure 4. Results of running HF/STO-3G optimization, followed by HF/6-31G* optimization calculations on the Set 1-4 molecules using both the geometry and the wavefunction guess.

and HF/6-31G* calculations converged. The second most common result (31, 20.7%) is that the HF/STO-3G converges, but the HF/6-31G* SCF fails on the first step. Other common scenarios is that the HF/STO-3G geometry optimization takes a bad step (17, 11.3%), the HF/STO-3G SCF fails to converge on the first step (14, 9.3%), the HF/STO-3G SCF fails to converge at a later geometry step (12, 8%), or that the HF/6-31G* fails to converge at a later step (7, 4.7%). Our analysis indicates that the convergence of 78 molecules in Sets 1-4 are improved if one of the STO-3G geometry or wavefunction is used, but only 62 molecules in Sets 1-4 are improved if one uses both the STO-3G geometry and wavefunction.

3.5 HF/6-31G* calculations using an HF/STO-3G geometry and wavefunction guess, with STO-3G Hessian calculation

We next examined calculations (20) for which the STO-3G geometry failed to converge, most of which took a bad step (17). Our initial thought was that the initial Hessian matrix was poor, so we used an analytical Hessian at the STO-3G level. None of the bad step calculations improved as the Hessian matrix eventually became small and/or negative. Of the remaining three calculations: CrP converged at both the HF/STO-3G and HF/6-31G* levels, the Ni_2 distance increased without bound as before, and the TiV failed to converge the SCF at some later step. Of the bad step calculations, use of an analytic frequency calculation at every step resulted in 11 of the 17 calculations finally converging at both the STO-3G and 6-31G* levels, with the remaining calculations having the same problem. This demonstrates that the problem is indeed related to the choice of Hessian during the optimization coupled with the too large bond distance choice. If these 20 calculations are run starting with a distance of 100 pm (1.0 Å) for the initial STO-3G structure, all converge at HF/STO-3G, and all except two converge at HF/6-31G*. For CoO, the SCF fails at a later HF/6-31G* step, and, for TiV, the SCF fails at the initial HF/6-31G* step.

4. Conclusions

For calculations on diatomic molecules at the HF/6-31G* level exhibiting convergence difficulties, successful convergence can often be achieved if either a HF/STO-3G wavefunction or optimized geometry, or both, are utilized. The STO-3G basis set remains a useful tool in the arsenal of the computational chemist.

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