Practical Advice for Quantum Chemistry Computations

C. David Sherrill
School of Chemistry and Biochemistry
Georgia Institute of Technology

Choice of Basis Set

- STO-3G is too small
- 6-31G* or 6-31G** probably give reasonable results; they may be better than cc-pVDZ
- For higher accuracy, try cc-pVTZ. Better than 6-311G**, etc.
- For benchmarks, probably want cc-pVQZ (but if you know enough to benchmark, you probably don't need my advice anymore…)
- For anions you must use diffuse functions (aug-, or +). Might also need them for excited states. Also need them for dispersion-bound complexes.
- Beyond Ne, you might want to try the cc-pV(X+d)Z basis sets
- For alkali or alkaline earth metals, you might want to correlate the (n-1) shell and use core-valence basis sets like cc-pCVXZ

Choice of Method

- Always pick DFT over HF; it's not much more expensive but usually gives much better results
- HF < DFT ~ MP2 < CCSD < CCSD(T) in general, but for some problems DFT can get lucky and do better than this
- MPn isn't guaranteed to converge, so don't bother with MP3, MP4, MP5, etc; use CC instead
- You should be an expert before you tackle unimolecular bond-breaking, diradicals, 3d transition metals --- these can all involve electronic near-degeneracies and might require CASSCF, CASPT2, etc. Blindly using DFT for these is dangerous.
- Standard HF, semiempirical, and DFT are not appropriate for van der Waals complexes or systems dominated by London dispersion forces

Common Things to Check

- Make sure your SCF procedure (HF or DFT) actually converges! If it doesn't, your calculation has failed (even if it didn't say so!). This is a root of many problems.
- For all other problems, check the point above first!

Making the SCF Converge

- Try upping the maximum number of SCF iterations
- If that doesn’t work, try using a smaller basis as an initial guess (this is almost required for large basis sets like aug-cc-pVTZ).
- For radicals or triplets, try adding a “level shift”. If that doesn’t work, you might try guess orbitals obtained from the nearest closed shell (i.e., the neutral singlet orbitals make a good guess for a radical cation computation).

Other Things to Check

- Make sure your geometry optimization actually converges. Otherwise, you don't have an optimized geometry!
- If the geometry converges, when possible, run a frequency computation to check that your geometry is really the type you want: a local minimum (with zero imaginary frequencies) or a transition state (with one and only one imaginary frequency).
- You can sometimes eliminate tiny, unwanted imaginary frequencies by tightening up the convergence criteria (integrals, SCF, correlation, and geometry criteria) or by making sure the correct symmetry is present in the computation
- Having more than 3N-6 (3N-5 for linear) vibrational frequencies is a sign you're not (quite) at a minimum; double-check and optimize tighter if necessary

Symmetry in Optimization

- If you start an optimization in a certain point-group, the molecule will be forced to stay in that point group (unless artifactual spatial symmetry breaking happens…). This can be good or bad, depending on your goals.
- If you get undesired significant (not noise) imaginary frequencies, this might be a sign the molecule wants to go to a lower symmetry but it couldn't because you started it with a high symmetry (the imaginaries will correspond to non-totally-symmetric irreducible representations). If this happens, distort the moleucle in the direction of the imaginary normal mode, and try again.

Efficient Optimizations

- If a geometry optimization is taking more than ~20 steps, you might need a more efficient approach
- Try computing a Hessian from a less expensive method, and reading that Hessian in for the optimization (particularly useful for TS searches)
- For van der Waals complexes, might be easier to optimize intermolecular coordinates by hand ---- normal optimizers are notoriously slow at this

Crazy Results

- If you get results that seem crazy for some reason (i.e., your computed excitation energies are negative, or your LUMO energy is negative and its not a cation, or vibrational frequencies are ridiculously high, or the SCF potential curve is discontinuous) one likely suspect is that you might have landed on the wrong SCF solution. This can happen for bond breaking, computations with very large basis sets, and/or very high symmetry
- You can check this in some programs by running a "stability analysis"

Orbital Occupations

- For programs that use symmetry, they have to guess the electron configuration (how many electrons in each irrep of the point group). Especially for large basis sets or complicated molecules, the programs can guess wrong and get stuck, giving the wrong "orbital occupations" and hence the wrong SCF energy.
- This is not always detectable by a SCF stability analysis.
- This problem frequently leads to unoccupied orbitals with negative energies, or occupied orbitals with positive energies. Try manually giving the orbital occupations (worked out by hand with group theory, or by guessing a new one based on the program's guess and looking at which orbitals seem to be swapped from their true order based on their energies).

Multiconfigurational Nature?

- Is your wavefunction questionable because of electronic near-degeneracies? There are diagnostics to check for this problem.
- Largest T2 amplitude: in MP2/CCSD, you can check your largest T2 amplitude. If it's around 0.1 or below, no problem. If it's much bigger (say, 0.2 or above), you may have a problem.
- There's also a "T1" diagnostic printed by some programs (Tim Lee, NASA). If it's > 0.02, you might have a multiconfigurational nature to the wavefunction and MP2/CC may be unreliable.
- MCSCF/CASSCF/CASPT2 are the solution (but are not black-box)