Towards an [almost] ‘black box’ RASSCF/RASPT2/SO-RASSI

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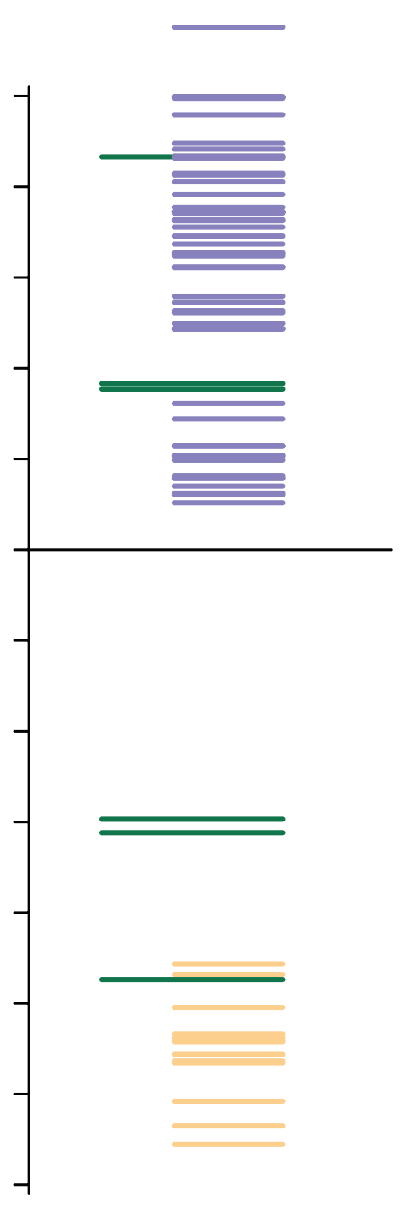
CASSCF and CASPT2 have become very useful tools in computational quantum chemistry (and occasionally combined with SO-RASSI for heavy elements), but they are difficult to use for non-experts.

In using these methods, the crucial problem is usually how to obtain or select a set of active orbitals. It has been shown in a number of studies that a large molecule does not necessarily imply the need for very many active orbitals. The problem is to select them.

Active orbitals

We are trying to find procedures that can aid in obtaining a good set of active orbitals. Ideally, such procedures could be 'mechanized', leading to 'black-box' methods. We are still far from such an outcome, but here is some of our experiences in selecting active orbitals.

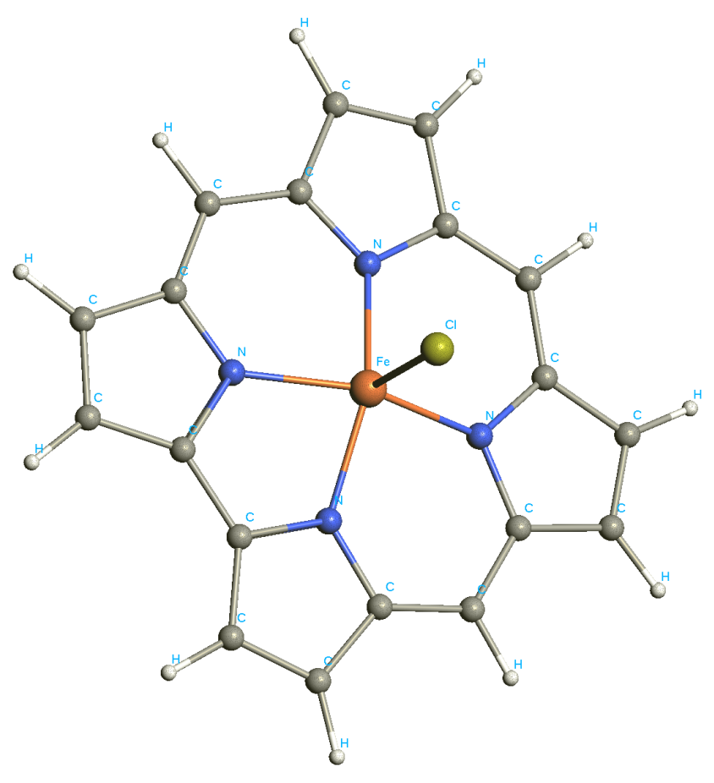
Orbital energies are usually worthless as a selection criterion: The orbitals that are best suited as active orbitals depend of course on the application, but generally one wants to have orbitals close to some active center, or orbitals that correlate efficiently with open shells, or with orbitals that differ much between spectroscopic states.



Examples:
Durene

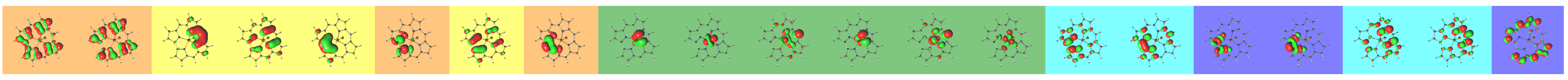
In the durene (1,2,4,5-tetramethylbenzene) example, the best choice of a small active space will span the six π-type atomic orbitals of the carbon atoms (green). The three strongly occupied ones will be an obvious choice; but the three correlating orbitals will be hidden deep into the virtual space. Choosing active orbitals as three HOMO and three LUMO orbitals may work, since the CASSCF orbital optimization may result in a proper choice even from a bad start, but often it does not. In this case, it does not, unless aided by symmetry.
But a simple RASSCF calculation with double excitations on 12 RAS1 and 12 RAS3 orbitals gives 6 orbitals with occupations numbers with highest deviations form 2 and 0. Graphical inspection of these orbitals shows that they have π-character and should be included into RAS2 active space.

FeCl-corrole

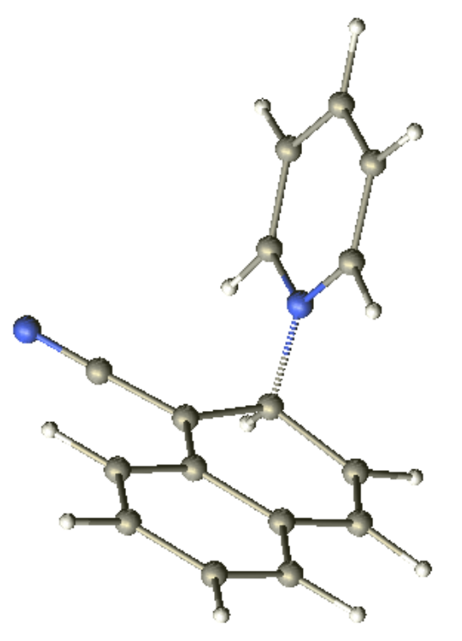


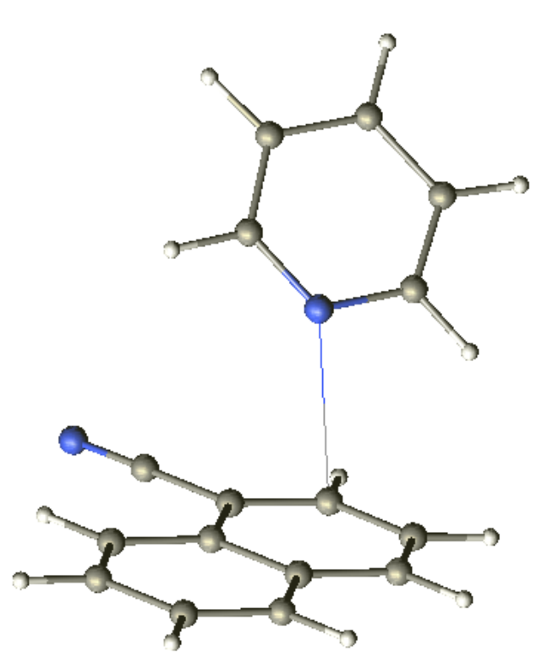
B. O. Roos has made a comprehensive study (private communication) of the performance of different active spaces for the spectroscopy of the iron complex FeCl-corrole, in the sense of working well for a number of states of different spin, ranging from singlets to septets. The best choice turned out to be one specific choice of 14 active orbitals with 14 electrons.
In retrospect, how well does a simple-minded approach work?

Minimal ANO basis, ACCD (Atomic Contracted Charge Decomposition) integrals, no symmetry. Initial calculations for five quintet states with RASSCF /4/6/4/ and 14 electrons were restarted for the two lowest quintet states with RASSCF /6/6/6/ and 18 active orbitals. The latter calculation converged in 63 iterations, which took 9h walltime on a PC.
The resulting 18 active orbitals has two pairs of strongly occupied sigma orbitals with the corresponding pair of correlating orbitals, with occupation numbers 1.98/0.02. These can be removed from the active space, leaving 14 electrons in 14 orbitals. (RAS1 - yellow, RAS2 - green, RAS3 - cyan).

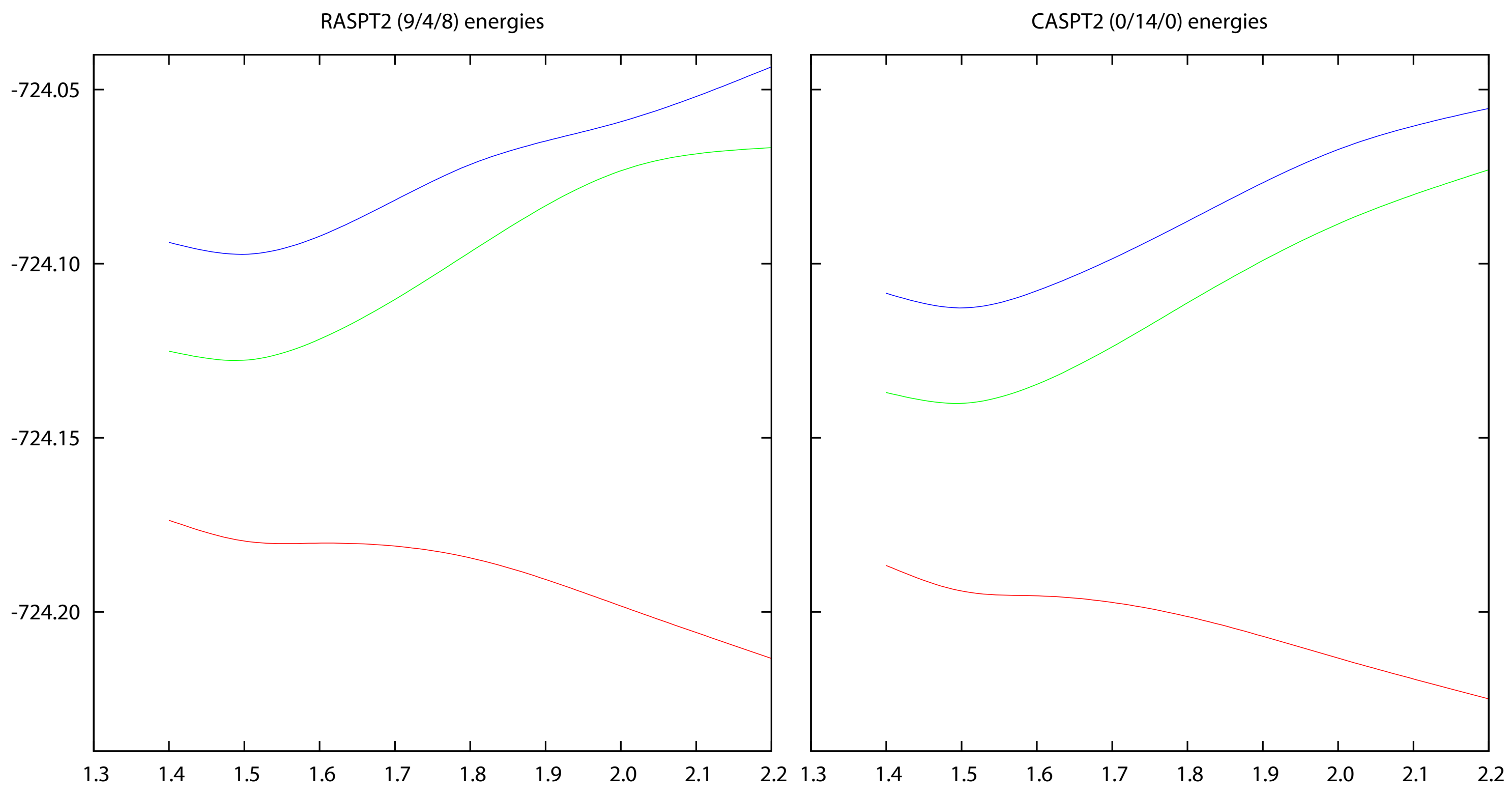


Pyridine-cyanonaphtalene





Pyridine and cyanonaphtalene can form an exciplex with distance 1.45 Å between the molecules, but a theoretical study requires a large active space. In this case, RASSCF/RASPT2 calculations with an active space /9/4/8/, i.e. 21 active orbitals, was shown (by comparison to the largest possible CASSCF/CASPT2 calculations) to give relative energies of comparable quality, and this RASSCF/RASPT2 calculation is of course much easier. Part of the reason for the large space is simply that different active orbitals are needed at different geometry and states. However, our interest in this approach for the moment is not so much for the calculation as such, but rather the fact that the cheaper RASSCF/RASPT2 approach seems to offer a good way of obtaining the active space. That the calculation is quite accurate already with this cheaper method is just a bonus.



Conclusions

Summarizing tools and techniques to be used in finding active space:
- A minimal basis set is usually sufficient for picking out starting orbitals. These can easily be expanded (by the EXPBAS tool) to a large basis for the production runs.
- Occupation numbers from cheap RASSCF with large large RAS1 and RAS3 are helpful.
- Graphical inspection of computed orbitals helps to select active space based on chemical intuition.
- Localized orbitals make the decision about the character of an orbital more straightforward.
- Orbital indicators should be developed to help recognize bonding and anti-bonding pairs of orbitals.

There is as yet no comprehensive solution to the active space problem for CASSCF, but there are some helpful approaches which has been or can be developed into software tools.

References

[1] MOLCAS homepage: ***http://www.molcas.org***
[2] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P.-Å. Malmqvist, P. Neogrády, T. B. Pedersen, M.Pitonák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh. Molcas 7: The Next Generation, *Journal of Computational Chemistry*, 2009. DOI: 10.1002/jcc.21318
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