

Constrained Unrestricted Hartree Fock and Single Excitation Configuration Interaction

Ruben Van der Stichelen

$$\langle \mathbf{G} | \mathbf{QC} | \mathbf{G} \rangle$$

Ghent University
April 23, 2021

1 Introduction

The Schrödinger equation allows us to express the energy of a wave function. However, since it is not exactly solvable for systems that have more than one electron, e.i. all most all things of importance, we are forced to make approximations. In these approximations we will deviate from reality by applying certain constraints that will allow us to solve the system. However, doing so will decrease the amount of freedom a system has to evolve. One might ask the question wheter we are not artificially creating something that behaves like it is reality, but acctually is nothing more than a construct. However if we do not impose constraints, we lose a lot of control, meaning that interpretation and data collection might jeopardized.

In this particular case we will take a look at the symmetry in the Hamiltonian. We know that in molecules there can be a lot of symmetry. This symmetry also exists in that molecules Hamiltonian, and thus also in every eigenfunction. Now we can easily state that every approximation we make of these eigenfunctions must contain that same symmetry. If we aspire to create somthing that is close to reality, but end up with something that does not have any real symmetry, we can do better. The important relation here is that the Hamiltonian commutes with the S^2 operator, meaning that these operators share a complete set of eigenfunctions. Thus an eigenfunction of the Hamiltonian must also be an eigenfunction of S^2 . This operator is responsible for the symmetry in a molecule.

In this paper we will discuss several modes in Hartree-Fock theory, focussed specifically on this symmetry. We will look at Restricted Closed Shell HF, Unrestricted HF, Constrained Unrestricted HF and in a minor capacity at Restricted Open Shell HF. We will compare the energies and wave functions and we will discuss using a symmetry argument why some energy might be higer than another. We will use Single excitation Configuration Interaction (CIS) to help in this analysis, as it will allow us to see multiplet excitation energies, which will indicate certain symmetries. If at all possible we will also attempt to visualise the orbitals obtained.

2 Hartree Fock Modes

In this section we will discuss the various Hartree Fock modes we have analysed over the course of this Bachelor project. For UHF and RHF we will not go into detail. CUHF will be discussed a little more rigourous, but not to the same level of detail as was done last year. ROHF will be discussed, but very superficial, since it is only needed as a comparative method. For every mode we will attempt to focus on the part that talks about symmetry. The final goal of this section then would be to explain for each mode where the symmetry comes from or why it is no longer there.

3 Single Excitation Configuration Interaction

The theory will be explained in detail, so that we can establish a good understanding of what it is and why we might want to do it. The focus will be on symmetry. We will also explain Brillouin's theorem. The question I would like to answer here is "Why are there triplets showing up in the excited states?"

4 results

I am not yet sure about the precise order here, but this section is divided in two parts.

4.1 H_2 stretch

Where we will display the plots of H_2 for all the modes, plotting spin contamination as well.

4.2 Excitations

Where we will discuss the datafiles as generated by the CIS molecule object. We would make plots of the various excitation energies, given that they are correct and I can figure out how to plot degenerate levels next to each other.

4.3 orbital diagrams

Given that I want to focus on symmetry, it might be nice to draw up orbitals. However I currently have no idea how.

5 conclusion

CUHF retains the symmetry, as can be seen in the datafiles. CUHF give different excitation energies than ROHF (has yet to be confirmed)

6 loose ends

I am not sure where to fit these PassOptionsToPackage

1. Determine point group for target molecule (allyl) and try to fit it into the results.