GHF

Release 0.1

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Nov 09, 2019

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CHAPTER

ONE

RESTRICTED HARTREE FOCK, BY MEANS OF SCF PROCEDURE

This class is used to calculate the RHF energy of a given molecule and the number of electrons. The molecule has to be created in pySCF: molecule = gto.M(atom = geometry, spin = diff. in alpha and beta electrons, basis = basis set)

class ghf.RHF.**RHF**(*molecule*, *number_of_electrons*)

Input is a molecule and the number of occupied orbitals.

Molecules are made in pySCF and calculations are performed as follows, eg.: The following snippet prints and returns RHF energy of h_2 and the number of iterations needed to get this value.

```
>>> h_2 = gto.M(atom = 'h 0 0 0; h 0 0 1', spin = 0, basis = 'cc-pvdz')
>>> x = RHF(h_2, 2)
>>> x.get_scf_solution()
Number of iterations: 109
Converged SCF energy in Hartree: -1.9403598392831243 (RHF)
```

get_last_dens()

Prints the last density matrix of the converged solution.

Returns The last density matrix.

get_last_fock()

Prints the last fock matrix of the converged solution.

Returns The last Fock matrix.

get_mo_coeff()

Prints the mo coefficients of the converged solution.

Returns The mo coefficients

get_one_e()

Returns The one electron integral matrix: T + V

get_ovlp()

Returns The overlap matrix

get_scf_solution()

Prints the number of iterations and the converged scf energy.

Returns The converged scf energy.

get_two_e()

Returns The electron repulsion interaction tensor

nuc_rep()

Returns The nuclear repulsion value

scf()

Performs a self consistent field calculation to find the lowest RHF energy.

Returns number of iterations, scf energy, mo coefficients, last density matrix, last fock matrix

CHAPTER

TWO

UNRESTRICTED HARTREE FOCK, BY MEANS OF SCF PROCEDURE

This class is used to calculate the UHF energy for a given molecule and the number of electrons of that molecule. Several options are available to make sure you get the lowest energy from your calculation, as well as some usefull functions to get intermediate values such as MO coefficients, density and fock matrices.

class ghf.UHF.**UHF**(*molecule*, *number_of_electrons*)

Input is a molecule and the number of occupied orbitals.

Molecules are made in pySCF and calculations are performed as follows, eg.: The following snippet prints and returns UHF energy of h_3 and the number of iterations needed to get this value.

For a normal scf calculation your input looks like the following example:

```
>>> h3 = gto.M(atom = 'h 0 0 0; h 0 0.86602540378 0.5; h 0 0 1', spin = 1, basis␣
↪= 'cc-pvdz')
>>> x = UHF(h_3, 3)
>>> x.get_scf_solution()
Number of iterations: 62
Converged SCF energy in Hartree: -1.5062743202681235 (UHF)
<S^2> = 0.7735672504295973, <S_z> = 0.5, Multiplicity = 2.023430009098014
```

extra_electron_guess()

This method adds two electrons to the system in order to get coefficients that can be used as a better guess for the scf procedure. This essentially forces the system into it's <S_z> = 0 state.

To perform a calculation with this method, you will have to work as follows:

```
>>> h4 = gto.M(atom = 'h 0 0 0; h 1 0 0; h 0 1 0; h 1 1 0' , spin = 2, basis␣
↪= 'cc-pvdz')
>>> x = UHF(h4, 4)
>>> guess = x.extra_electron_guess()
>>> x.get_scf_solution(guess)
Number of iterations: 74
Converged SCF energy in Hartree: -2.0210882477030547 (UHF)
<S^2> = 1.0565277001056579, <S_z> = 0.0, Multiplicity = 2.2860688529487976
```

Returns A new guess matrix to use for the scf procedure.

get_last_dens()

Gets the last density matrix of the converged solution. Alpha density in the first matrix, beta density in the second.

Returns The last density matrix.

get_last_fock()

Gets the last fock matrix of the converged solution. Alpha Fock matrix first, beta Fock matrix second.

Returns The last Fock matrix.

get_mo_coeff()
Gets the mo coefficients of the converged solution. Alpha coefficients in the first matrix, beta coefficients in the second.

Returns The mo coefficients

get_one_e()

Returns The one electron integral matrix: T + V

get_ovlp()

Returns The overlap matrix

get_scf_solution(*guess=None*)
Prints the number of iterations and the converged scf energy. Also prints the expectation value of S_z, S^2 and the multiplicity.

Returns The converged scf energy.

get_two_e()

Returns The electron repulsion interaction tensor

nuc_rep()

Returns The nuclear repulsion value

scf(*initial_guess=None*)
Performs a self consistent field calculation to find the lowest UHF energy.

Parameters **initial_guess** – A tuple of an alpha and beta guess matrix. If none, the core hamiltonian will be used for both.

Returns The scf energy, number of iterations, the mo coefficients, the last density and the last fock matrices

stability()
Performing a stability analysis checks whether or not the wave function is stable, by checking the lowest eigen- value of the Hessian matrix. If there's an instability, the MO's will be rotated in the direction of the lowest eigenvalue. These new MO's can then be used to start a new scf procedure.

To perform a stability analysis, use the following syntax:

```
>>> h4 = gto.M(atom = 'h 0 0 0; h 1 0 0; h 0 1 0; h 1 1 0' , spin = 2, basis␣
↪= 'cc-pvdz')
>>> x = UHF(h4, 4)
>>> guess = x.stability()
>>> x.get_scf_solution(guess)
There is an internal instability in the UHF wave function.
Number of iterations: 78
Converged SCF energy in Hartree: -2.0210882477030716 (UHF)
<S^2> = 1.056527700105677, <S_z> = 0.0, Multiplicity = 2.2860688529488145
```

Returns New and improved MO's.

CHAPTER

THREE

REAL GENERALISED HARTREE FOCK, BY MEANS OF SCF PROCEDURE

This function calculates the real GHF energy for a given molecule and the number of electrons in the system. The molecule has to be created in pySCF: molecule = gto.M(atom = geometry, spin = diff. in alpha and beta electrons, basis = basis set)

The function can do this in two ways.

- Create the general density matrix and work with this as a whole
- create the density matrix in spin-blocked notation

ghf.real_GHF.**real_GHF**(*molecule*, *number_of_electrons*)

Input is a molecule and the number of electrons.

Molecules are made in pySCF, eg.:

```
>>> h_2 = gto.M(atom = 'h 0 0 0; h 0 0 1', spin = 0, basis = 'cc-pvdz')
>>> GHF(h_2, 2)
```

prints and returns GHF energy of h_2

CHAPTER

FOUR

USEFUL FUNCTIONS FOR SCF PROCEDURE

A number of functions used throughout the UHF and RHF calculations are summarised here.

ghf.SCF_functions.**density_matrix**(*f_matrix*, *occ*, *trans*)

- density() creates a density matrix from a fock matrix and the number of occupied orbitals.
- Input is a fock matrix, the number of occupied orbitals, which can be separate for alpha and beta in case of UHF.

And a transformation matrix X.

ghf.SCF_functions.**get_integrals**(*molecule*)
A function to calculate your integrals & nuclear repulsion with pyscf.

ghf.SCF_functions.**spin**(*occ_a*, *occ_b*, *coeff_a*, *coeff_b*, *overlap*)

Parameters

- **occ_a** – number of occupied alpha orbitals
- **occ_b** – number of occupied beta orbitals
- **coeff_a** – MO coefficients of alpha orbitals
- **coeff_b** – MO coefficients of beta orbitals
- **overlap** – overlap matrix of the molecule

Returns S^2, S_z and spin multiplicity

ghf.SCF_functions.**trans_matrix**(*overlap*)

- Define a transformation matrix X, used to orthogonalize different matrices throughout the calculation.
- Input should be an overlap matrix.

ghf.SCF_functions.**uhf_fock_matrix**(*density_matrix_1*, *density_matrix_2*, *one_electron*, *two_electron*)

- calculate a fock matrix from a given alpha and beta density matrix
- fock alpha if 1 = alpha and 2 = beta and vice versa
- input is the density matrix for alpha and beta, a one electron matrix and a two electron tensor.

ghf.SCF_functions.**uhf_scf_energy**(*density_matrix_a*, *density_matrix_b*, *fock_a*, *fock_b*, *one_electron*)

- calculate the scf energy value from a given density matrix and a given fock matrix for both alpha and beta, so 4 matrices in total
- then calculate the initial electronic energy and put it into an array

- input is the density matrices for alpha and beta, the fock matrices for alpha and beta and lastly a one electron matrix

CHAPTER

FIVE

TESTING THE RHF AND UHF METHODS

Simple tests to check whether or not the functions return the correct value.

ghf.tests.test_auth.**test_RHF**()
: test_RHF will test whether or not the RHF method returns the wanted result. The accuracy is 10^16.

ghf.tests.test_auth.**test_UHF**()
: test_UHF will test the regular UHF method, by checking whether or not it returns the expected result. The accuracy is 10^-6.

ghf.tests.test_auth.**test_extra_e**()
: test_extra_e will test the UHF method, with the added option of first adding 2 electrons to the system and using those coefficients for the actual system, by checking whether or not it returns the expected result. The accuracy is 10^-6.

ghf.tests.test_auth.**test_stability**()
: test_stability will test the UHF method, with stability analysis, by checking whether or not it returns the expected result. The accuracy is 10^-6.

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