Computational Quantum Physics
Exercise 5

PHYS-463
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Problem 5.1 Molecular energies using PySCF

In this exercise we will compute the dissociation curve of the molecule H_2 using the Python library for quantum chemistry PySCF.

a) Follow the tutorial to compute the equilibrium energy of H_2 using the Hartree-Fock (HF) and the Full Configuration interaction (FCI) method in the STO-3G minimal basis.

b) Now apply the above code to compute the dissociation curve of H_2 with HF and FCI in the STO-3G minimal basis.

What are the qualitative differences between the HF and the FCI curves? What do those differences indicate?

Hint: To compute the dissociation curve, obtain the HF and FCI energy placing the two atoms at different distances d.

c) Compute the dissociation curve with different basis set (STO-6G, 6-31g, cc-pVDZ, ...) and see how the dissociation curves change. What can be said about the curves obtained with HF? And with FCI?

Problem 5.2 Molecular energies using Hartree-Fock

In this exercise we compute the energy of the H_2O molecule at the equilibrium geometry using the spin-restricted Hartree-Fock method. To this end we follow the procedure described in Section 6.4.4 of the lecture notes.

a) Use PySCF to compute the integrals for the overlap matrix S as well as the coefficients t_{ij} and V_{ijkl} of the one- and two-body terms of the Hamiltonian, using the cc-pVTZ basis set for the f_α basis functions.

b) Write a function which, given a set of coefficients C, computes the density matrix P, the fock Matrix F and returns the new set of coefficients given by the solution of the Roothan-Hall equation (Eq. 6.45 in the lecture notes).

$$\sum_\beta (F_{\alpha\beta} - \epsilon_k S_{\alpha\beta}) C_{\beta k} = 0$$

Hint: Use 'scipy.linalg.eigh' to solve the generalized eigenvalue problem directly, without having to convert it to a standard eigenvalue problem.

c) Run the self-consistent procedure, calling b) repeatedly until convergence to the fixed point is reached, initializing the coefficients C randomly.

d) Compare your results to a Hartree-fock calculation done with PySCF.