



ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Written Exam
Introduction to Electronic Structure Methods
(Autumn Semester 2012)

Family Name:

First Name:

1. All standard quantum chemical electronic structure methods are based on three basic assumptions. Which ones? How/when are they justified and when not?
2. Show that a hypothetical Slater determinant
$$\Psi = 1/\sqrt{2} |\varphi_{1s}^{\alpha}(1)\varphi_{1s}^{\alpha}(2)|$$
for a He atom is identical to zero.
3. How many basis functions are included in a calculation of the molecule NH_3 with the basis set 6-311G**? From how many primitive Gaussians is this basis constructed?
4. What is the Basis Set Superposition Error (BSSE)? How can one avoid/correct BSSE? In which systems is the BSSE a particularly serious problem?
5. According to Hund's rule, states with maximum spin multiplicity are energetically preferred. Give a justification of this empirical rule based on the Hartree-Fock energy expression

$$E_{HF} = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} [ii|jj] - [ij|ji]$$

6. Why is the Hartree-Fock method sometimes called SCF (self consistent field)?

Bonus: Explain the terms 'restricted', 'unrestricted' and 'restricted-open shell' Hartree-Fock calculations.