# Discussion on quantum chemical methods

*Emmanuel Fromager*

UNIVERSITÉ DE **STRASBOURG**

cnrs

Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique - Université de Strasbourg /CNRS

M2 lecture, Strasbourg, France.

- What is the Born–Oppenheimer approximation ? Are the nuclei treated in classical mechanics within such an approximation ? How are vibrational energies and electronic energies related ?

- What is the key idea underlying the Hartree–Fock (HF) approximation ? What is the definition of the correlation energy? Is FCI exact ?

- What are the main differences between the first and second quantization formalisms ? How is the Pauli principle formulated in second quantization ?

- What is the main difference between variational and non-variational quantum chemical methods ?

- Explain why the HF method can be formulated as an orbital rotation problem. How can the HF orbitals be optimized? How can we verify in a CI calculation that the determinants are constructed from HF orbitals? If we perform the FCI calculation with different molecular orbitals [the KS orbitals, for example] without changing the atomic orbital basis, do we obtain a different FCI energy?

- What are the various strategies used in wavefunction theory for modelling dynamical electron correlation ? What are the advantages and drawbacks of theses strategies ?

- In MP2, which excitations contribute to the energy through second order ?

- What is the motivation for using a Coupled-Cluster (CC) ansatz for the wavefunction ?

- Is there a difference between CISD and CCSD for a two-electron system ?

- Define the concept of static correlation. What is the appropriate method for its description ? How is the wavefunction parameterized within this method ? Is it possible to describe excited states with this method ? Does it provide accurate results ?

- In the stretched $H_2$ molecule, chemists refer to static correlation as "left-right correlation". Why ? Why do physicists refer to it as "strong correlation" ? Why do they interpret it as a short-range correlation effect ?

- Does the energy depend explicitly on the electron density ?

- Are the excited-state energies functional of the ground-state density ? Is it straightforward to calculate excited-state energies in DFT ? Is there a variational principle for excited states ?

- What are the differences and similarities between HF and Kohn–Sham (KS) density-functional approaches ?

- Is it possible to describe ground-state electronic structures exactly with one single electron configuration ?

- The local density approximation (LDA) fails in describing both bond dissociations and dispersion forces. What is the reason ? Does it mean that KS-DFT can only be applied to some electronic systems but not all ?