**Quantum Chemistry Methods for Predicting and Interpreting Nonlinear Optical (NLO) Properties**

**Benoît CHAMPAGNE**

**Krakow (Poland), 2014-2015 (1st semester) – 40 H**

**Wednesday 22nd afternoon**

**I. Context, definitions, and motivations (1/2 H)**

**II. Elements of quantum chemistry (1/2 H)**

II.A. From the Born-Oppenheimer approximation to the HF method

**III. (Hyper)polarizability expressions (1 H)**

**IV. (Hyper)polarizabilities as responses properties (2H)**

IV.A. The CPHF scheme

IV.B. The FF method

IV.C. The TDHF scheme

**Thursday 23rd morning**

**Computer Lab 1**: How to choose the field amplitude in a Hartree-Fock/Finite Field calculation of the polarizability, first and second hyperpolarizabilities of *p*-nitroaniline ? – comparison with the CPHF methods **(3H)**.

**Thursday 23rd afternoon**

**V. Electron correlation effects (4H)**

V.A. Wavefunction methods (MPPT, CI, CC)

V.B. Response approaches at the correlated level

V.C. DFT and TDDFT response methods

V.D. Wavefunction methods and basis set effects on  and 

1. Small molecules

2. Large molecules

V.E. Assessment of DFT approaches

1. Extended systems

2. Small/reference molecules

3. Molecular switches

**Friday 24th [the results will be analyzed later]**

**Computer Lab 2**: Effect of the basis set on the polarizability, first and second hyperpolarizabilities of formaldehyde and *p*-nitroaniline **(3H)**

**Wednesday 5th afternoon**

**VI. (Hyper)polarizabilities from perturbation theory (3H)**

VI.A. Rayleigh-Schrödinger PT

VI.B. Basic SOS expressions

VI.C. SOS/CI expressions

VI.D. Variations on the SOS expressions

**Thursday 6th morning [+ discussion on basis set effects]**

**Computer Lab 3**: Effect of electron correlation (wavefunction and DFT) on the polarizability, first and second hyperpolarizabilities of formaldehyde and *p*-nitroaniline **(3H)**

**Thursday 6th afternoon**

**VII. Illustrations dealing with  (3H)**

VII.A. D/A effects on 

VII.A. Size and shape effects on 

VII.B. Molecular switches

**Friday 7th afternoon**

**VIII. Illustrations dealing with  (3H)**

VIII.A. of π-conjugated systems, BLA and size effects

VIII.B. D/A effects on

VIII.C. of open-shell systems

**Friday 7th morning**

**Computer Lab 4**: Designing π-conjugated systems with large first and second hyperpolarizabilities – choice of the nature and position of the substituents **(3H)**

**January 2015 (probably 26th to 29th – to be announced)**

**IX. Vibrational hyperpolarizabilities (4H)**

I.X.A. Bishop-Kirtman perturbation theory

I.X.B. ∞-optical frequency approximation

I.X.C. FF-NR scheme and FIC

I.X.D. Zero-point vibrational average contributions

I.X.E. Illustrations on the importance of the vibrational contributions

**Computer Lab 5**: Electronic versus vibrational polarizabilities, first and second hyperpolarizabilities of formaldehyde and *p*-nitroaniline **(3H)**

**X. Effects of the surrounding (4H)**

X.A. Solvent

X.B. Solid state

**Vibrational spectroscopies and their simulations**

**Benoît CHAMPAGNE**

**Krakow (Poland), 2014-2015 (2nd semester) – 20 H**

**I. Vibrational frequencies and normal modes**

I.A. Hessian and force constants

I.B. Anharmonicity corrections

**II. IR, Raman, and hyper-Raman spectroscopy**

**III. Sum-Frequency generation (SFG)**

**IV Chirality-related techniques (VCD & VROA)**

**V. Resonance spectroscopies (RR, RhR, and DR-SFG)**