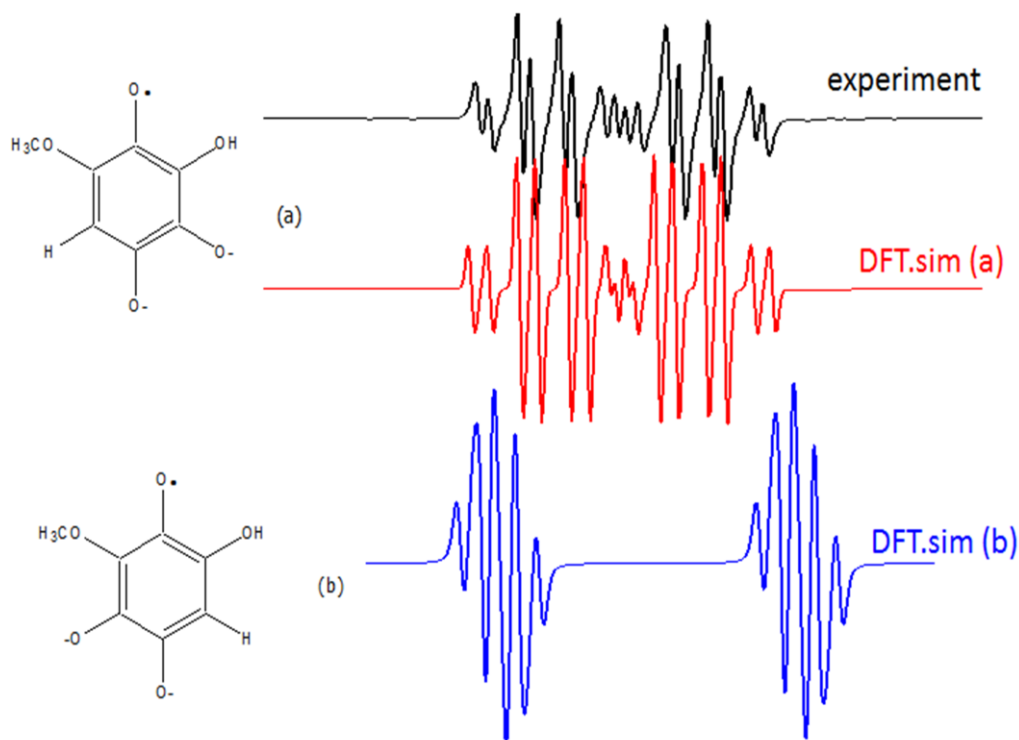


Compounds with an additional electron in their electronic structure are known as “radical” forms. These kinds of chemicals can be experimentally measured using Electron Paramagnetic Resonance (EPR) spectroscopy. This unpaired electron is loosely bounded so it actively contributes in chemical reactions. Considering that an electron can be defined via its wave function in a quantum mechanical concept, one may say that EPR spectroscopy provides the experimental tool for measuring the wave function of the unpaired electron. So there is a close relationship between the theoretical and experimental parts of such studies.

Our goal is to calculate the magnetic properties (means EPR hyperfine couplings and g-values in our case) of compounds by using quantum chemical tools. Such calculations enable you to identify your radical sample by comparison with experimental data and make predictions about the behavior of similar systems.

As an instance, Simulation of an EPR spectrum of a solvated Quinone compound in alkaline media, gives some information about the functional groups which you have in your product compound, like a methoxy, a hydroxyl and a proton. Now the question is that the position of these groups relative together. Calculations using Density Functional Theory (DFT) give a clear identification for model (a).



During your study, you find the most affecting factors on the MO which carries the unpaired electron (known as SOMO) , spin density distribution of the unpaired electron by which you can calculate the hyperfine and g-tensors of the system (like nitrogen based radicals, trityl radicals or protected spin lables ). For this purpose, you use DFT methods as implemented in "Gaussian" software package.

Time schedule:

Week 1: Basic EPR calculations

Week 2-4: project theme

Week 5-6: data analysis

Week 7-8: writing

References:

Here you find some useful references. Some of them provide you with theoretical background and some other show the applications.

1-Calculation of NMR and EPR parameters: theory and applications, M. Kaupp, M. Bühl, V. G. Malkin, Wiley-VCH (2004).

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3- Theory of isotropic hyperfine interactions in pi- electron Radicals ,H.M. McConnell and D. B. Chesnut, (1958), J. Chem. Phys. 28, 107-117.

4-DFT study of nitroxide radicals: explicit modeling of solvent effects on the structural and electronic characteristics of 4-amino-2,2,6,6-tetramethyl-piperidine-*N*-oxyl,L.N. Ikryannikova, L.Yu. Ustynyuk and A.N. Tikhonov, Magn. Reson. Chem.(2010) 48, 337–349.

5- Effect of hydrogen bonding on the spin density distribution and hyperfine couplings of the p-Benzosemiquinone anion radical in alcohol solvents: a hybrid density functional study, P.J. O'Malley, J. Phys. Chem. A (1997)101, 9813-9817.

6- Solvent effects on g-tensors of semiquinone radical anions: polarizable continuum versus cluster models, I.Ciofini, R. Reviakine, A. Arbuznikov,M.Kaupp. (2004) 111, 132-140.

7- Interplay of electronic, environmental, and vibrational effects in determining the hyperfine coupling constants of organic free radicals. R.Improta, V.Barone, Chem Rev.(2004) 104, 1231-1254.

8-The metal carbon double bond in Fischer carbenes: a density functional study of the importance of nonlocal density corrections and relativistic effects, H.Jacobsen, G.Schreckenbach and T.Ziegler, J. Phys. Chem. (1994) 98, 11406-11410.