Laboratoire de Chimie et Physique Quantiques

AGENCE NATIONALE DE LA RECHERCHE ANR

Université de Toulouse

PhD position in Quantum Chemistry in Toulouse (France)

Calculation of pNMR shifts in actinide complexes

Work description

The doctoral student will work on the computation with first principles methods and the modelisation of paramagnetic NMR shifts in actinide complexes. The work will take place in Toulouse, in SEM group of the Laboratoire de Physique et de Chimie Quantiques and will be performed in close collaboration with the experimentalists of the team of Claude Berthon, in CEA Marcoule (France) and with Autschbach's group in Buffalo (US) which develops new quantum chemistry tools. The student will spend one month in Autschbach's group during his/her thesis.

Summary

Paramagnetic NMR (pNMR) measures the NMR shift of paramagnetic complexes compared to their diamagnetic counterpart. This shift may be split into a *contact* term and a *pseudo-contact* term. The pseudo-contact term arises from the dipolar magnetic interaction between the electronic magnetic moment of the paramagnetic center and the nuclear magnetic moment of the nucleus of interest, while the contact term is caused by a non zero spin density at the nucleus and is a signature of a spin density delocalization between the metal center and the ligand: it probes the degree of covalency between the paramagnetic center and the ligand.

First principles calculations on actinide based complexes are challenging since they gather together many of the difficulties of quantum chemistry : i) these complexes, when magnetic, are open-shell and should be described by multiconfigurational methods. ii) since actinides are at the bottom of the classification table, relativistic effects must be included in the calculations, both scalar and spin-orbit. iii) Contrarily to lanthanides, dynamical correlation play a key role for actinides : correlated methods must be used in order to get quantitative results. The calculation of pNMR shifts from first principles adds two more difficulties to the usual calculation of electronic magnetic properties: the coupling with the nuclear spin momenta through the hyperfine coupling and the delocalisation of the spin density on the whole molecule in order to describe propertly the contact term. It necessitates an accurate description of both the anisotropic magnetic properties of the paramagnetic center, and of the delocalisation of the spin density on the ligands, since the contact shielding is caused by a non-zero spin density at the nucleus of interest.

The aim of the thesis is to perform first principles calculations of pNMR shifts in actinide series synthesized and probed by NMR in the group of Claude Berthon using methods newly developped by the team of Jochen Autschbach. Finally, results will be rationalized using an effective model.

Applicants :

Applicants should be graduated in physics, physical chemistry or chemistry. Theoretical and mathematical abilities are necessary in order to carry out the project. Good knowledges in theoretical chemistry and inorganic chemistry will be beneficial. Solid English skills (both written and oral) are mandatory, knowledge of (or the willingness to learn) French is a plus.

To apply :

Interested candidates should send a full CV, a letter of motivation, contact data for two references and a copy of their master's degree and a copy of their last university degrees by e-mail to bolvin@irsamc.ups-tlse.fr
Application deadline: until the position is filled.

Location
Laboratoire de Chimie et de Physique Quantiques Université Toulouse III
http://www.lcpq.ups-tlse.fr

Supervisors
Hélène Bolvin: bolvin@irsamc.ups-tlse.fr
Nicolas Suaud: suaud@irsamc.ups-tlse.fr

Postion:
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