

Abstract:

In the last three decades, the studies of organometallic complexes containing heavy metals of element f (lanthanides and actinides) have been widely explored; this field is experiencing a remarkable state of progress on the experimental and theoretical levels, particularly for bimetallic complexes. This type of complexes recently synthesized with interesting properties, such as magnetic properties which are of great interest from the point of view of fundamental research and technological application as single molecular magnet or SMM which are integrated in the development of digital information storage.

One of the main goals of this field is to understand the factors that control and affect the interactions between the magnetic sites of two metals linked by an aromatic ligand. For this we need to know the electronic and magnetic structures of these objects. Theoretically, the use of relativistic density functional theory gives many possibilities to study those chemical systems that contain a large number of electrons.

The study of f-element complexes shows that they have structural and electronic properties not known in transition metal chemistry, these properties indicating metal-ligand interactions depending on the relativistic effects of heavy metals.

Most important think in these studies is to understand the role of the d and f valence orbitals of the metal to create metal-ligand bond and the nature of the metal bond in these complexes so as to rationalize their physical and chemical properties. But there are always difficulties found in carrying out the experimental studies due to many obstacles such as radiotoxicity and the scarcity of the raw material and sometimes the high budget. Carry out theoretical studies. Nevertheless, it remains to find solutions concerning calculation methods and computer tools, for example systems involving a very high number of electrons require very large memory capacities and a very high calculation time that can reach several months for a single complex. Without forgetting the correlations problems and relativistic effects.

The present work has been developed since 2014, we are interested in applying the density functional theory (DFT) in the study of the modeling and the determination of the magnetic properties of bi-nuclear organometallic complexes of element f, as well as theoretical studies applied in the form of theoretical calculations at the level of the ADF calculation program (Amsterdam density functional).

We can say that these studies are mainly devoted to the quantification of the spin-spin exchange coupling constant within the bimetallic molecular complexes of uranium (IV) and (V), the study of the properties and magnetic behavior and the modeling of the coupling of these complexes containing two metallic centers of uranium bound together by an aromatic bridging ligand, which exhibits anti and ferromagnetic exchange interactions.

Therefore, our objective is to understand the role of metal f orbitals in the creation of metal-ligand chemical bonds and the properties of the compounds studied. The method used is based on the theory of the functional of the density "DFT", by taking into account the relativistic effects by the approximation ZORA (Zeroth Order Regular Approximation) coupled with the method of the broken symmetry of the spin "BS". This DFT/ZORA/BS method has proven itself for this type of study and treatment of the properties of this type of system.

After several years of work, we were able to collect and extract the results obtained in this thesis which consists of several parts, which include an introduction and a general conclusion with four talking chapters on our research subject.

The first chapter entitled (Theoretical and methodological aspect) contains the theoretical aspects and the methodology of quantum chemistry, the important relativistic effects, the approximations and the approaches for this study to carry out.

The second chapter takes up the concepts and the fundamental relations of the theories applied in quantum chemistry, which allowed us to obtain these results, and which explains the field of the magnetic fields and the exchange coupling, the different approaches which helped us to model and study the magnetic coupling as the method of broken symmetry BS (Broken symmetry), the methods and the techniques of the realization of the calculations. This chapter entitled (Molecular magnetism, general concept).

Constitute the essence of the results obtained within the framework of this doctoral thesis. The third chapter entitled (relativistic DFT study of magnetic coupling in the diuranium U(IV)-U(IV) ethynediyl-bispyrazine and imino-amido quinoid complexes.) we were interested in studying the ferro or antiferromagnetic magnetic character of di-uranium U(IV) of the $5f^2-5f^2$ configuration, linked by two different types of aromatic bridge. the model ethynediyl-bispyrazine diuranium $[\text{Cp}_3\text{U}]_2(\text{ethyne-1,2-diyl})\text{bis}(\text{pyrazi-4-ide})$ an unsynthesized typical example showing significant magnetic properties, the second complex is imino-amido quinoid diuranium which is recently synthesized and which gives results and behaviors in agreement with experimental, these two complexes present an

antiferromagnetic behavior, we carried out calculations DFT/ZORA/B3LYP coupled with the approach Broken Symmetry (BS) to try to explain the magnetic behavior of two compounds.

We have enriched our theoretical study with a fourth chapter under the title (Electronic structure and magnetic properties of bridged diuranium(V) naphthalene and stilbene-diimide complexes: a theoretical study.) which speaks about the study of the other two molecular pentavalent systems U(V) uranium bis metal of the $5f^1-5f^1$ configuration. In this chapter we have provided a theoretical study of two paramagnetic complexes naphthalene-diimide $[(MeC_5H_4)_3UV]_2(\mu-1,5-N_2C_{10}H_6)$ and stilbene-diimide $[(MeC_5H_4)_3UV]_2(\mu-1,2-(4-NC_6H_4)_2-C_2H_2)$, and which have no systematic theoretical study to date. These systems were synthesized and rationalized from an experimental result obtained by Rosen et al. in 1989 but their magnetic behaviors were not entirely demonstrated by susceptibility measurements. Both complexes exhibit antiferromagnetic behavior in the U(V)—L—U(V) superexchange interaction.

The results obtained confirm the effectiveness of the method used in all respects, since it is consistent with the published experimental results.

Keywords: magnetic properties, spin-spin coupling, DFT, spin broken symmetry, organometallic compounds, uranium.