



# COPPER(II) COORDINATION COMPOUNDS CORRELATIONS WITH ATOMIC DESCRIPTORS

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## Abstract

The main goal of this project is to produce a model that is both explanatory and predictive of two chemical relevant copper(II) properties. The first property is the formation equilibrium of copper(II) coordination compounds (experimental) and the second is a descriptor that describes the polarization in metallic atoms (*AGD*). With a constructed database of Cu(II) complexes we proposed two models of these properties which depend on descriptors calculated in a QTAIM scheme. The model of the formation constant shows that this property will tend to be higher as the basicity from the copper atom increases and with more nucleophilic ligands. On the other hand, the *AGD* descriptor model shows that this descriptor is related with changes in the electron density form and  $\alpha$ ,  $\beta$  populations.

## Introduction

### Atomic Properties

The Quantum Theory of Atoms in Molecule proposes a partition scheme of the electron density ( $\rho(\mathbf{r})$ ) of a molecule, such that each partition ( $\Omega$ ) corresponds to an atom [1]. With this partition scheme it is possible to define electronic properties of an atom inside a molecule. For instance:

- Electronic populations ( $\sigma \equiv \alpha$  or  $\beta$ ) [2]:  $N_\sigma(\Omega) = \int_\Omega \psi_i^{\sigma*}(\mathbf{r}) \psi_i^\sigma(\mathbf{r}) d\mathbf{r}$
- Atomic quadrupole moments: Symmetric tensor in which each component measures if the atomic electron density is concentrating ( $Q < 0$ , Prolate) or depleting along a certain direction ( $Q > 0$ , Oblate). [3]

### Electronic Laplacian and *AGD*

In essence,  $\nabla^2 \rho(\mathbf{r})$  determines concentrated (basic or nucleophilic) or depleted regions (acid or electrophilic) of an atom [3]. The critical points of  $\nabla^2 \rho(\mathbf{r})$  form a pictorial representation of a connectivity scheme called the Atomic Graph [1, 3]. An atomic descriptor has been previously proposed that, in theory, reflects the polarization of a central metallic atom based on its Atomic Graph [4]. This descriptor is represented by Eq (1) and the Atomic Graph from Copper(II) is shown in Fig (1).

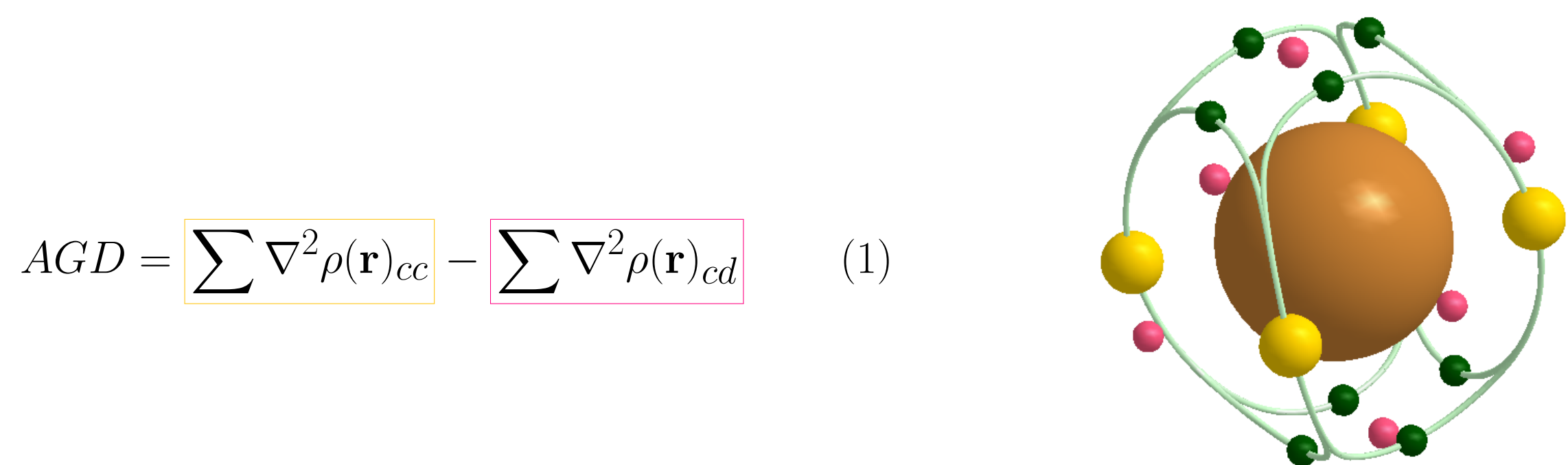
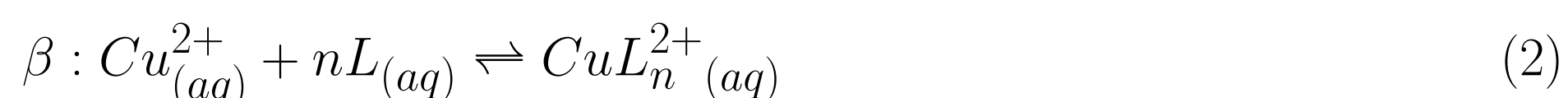


Fig. 1: Atomic Graph: 4 Concentration(Yellow) and 6 Depletion(Pink) CPs

### Formation Constant of Complexes

The experimental value, most commonly used to describe the thermodynamic aspects of metal-ligand interactions, is the formation constants of complexes [6]. These constants represent thermodynamic equilibria between a metal nuclei and a given a number of ligands as represented in the Eq (2) [5].

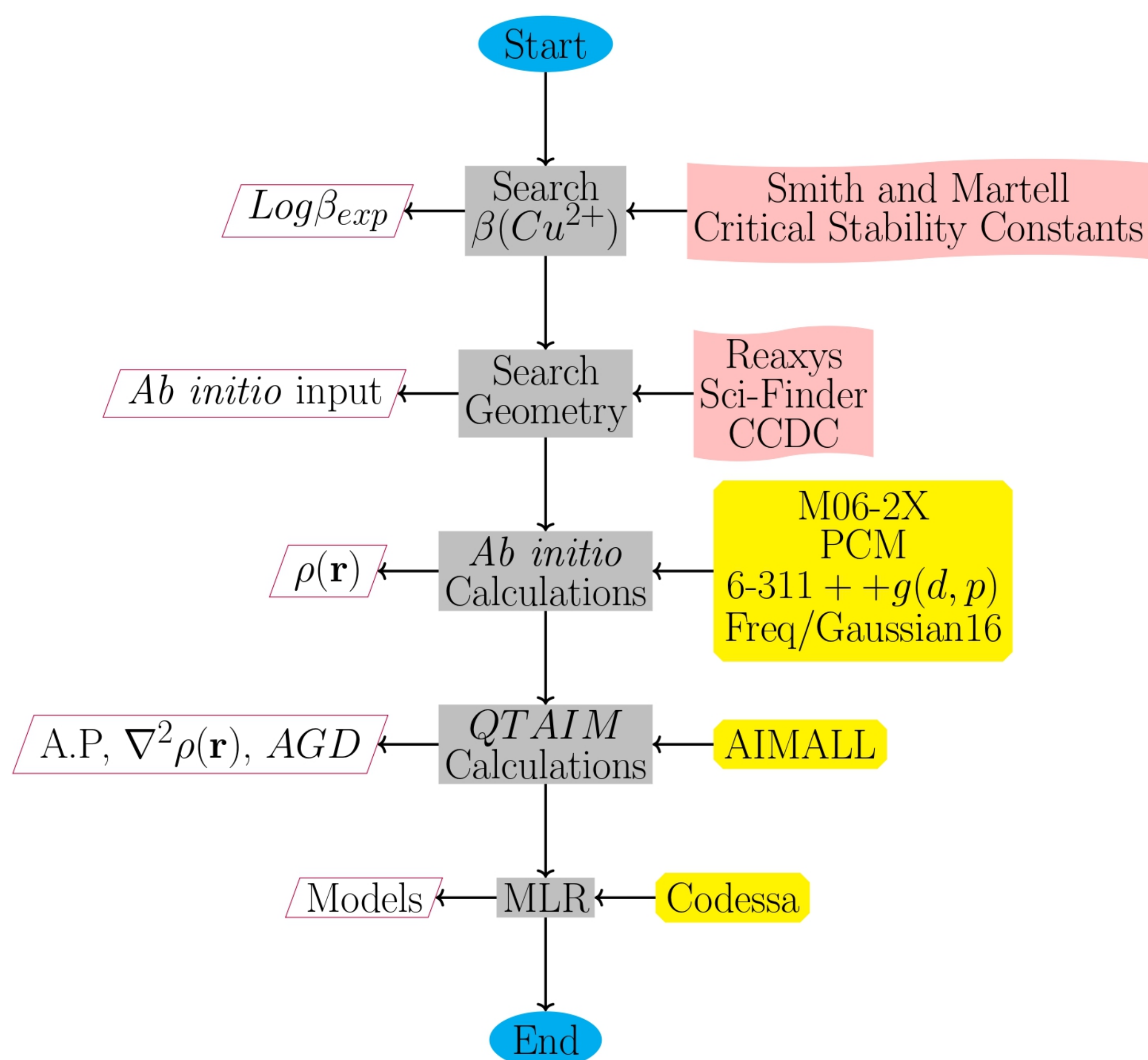


This thermodynamic constant is reported as  $Log\beta_{exp}$  and is used to design and understand new complexes and its reactivity [6]

## Objectives

- To produce a predictive and explanatory model:  $\rightarrow Log\beta_{exp} = f(Descriptors)$
- To produce a predictive and explanatory model  $\rightarrow AGD = f(Descriptors)$

## Method



## Results

### Models for the Formation Constant of Complexes

We find the following model for the copper formation constants (The equations are color labeled according to the CPs considered in Fig (1) and Fig (3) )

$$Log\beta_{exp} = -0.314 \sum \nabla^2 \rho(\mathbf{r})_{cc}(NO)^{\{Fig\ 3\}} - 0.507 \sum \nabla^2 \rho(\mathbf{r})_{cc}(Cu)^{\{Fig\ 1\}} + 0.081 \sum \nabla^2 \rho(\mathbf{r})_{cd}(Cu)^{\{Fig\ 1\}} + 88.369N(Cu) - 2656.510 \quad (3)$$

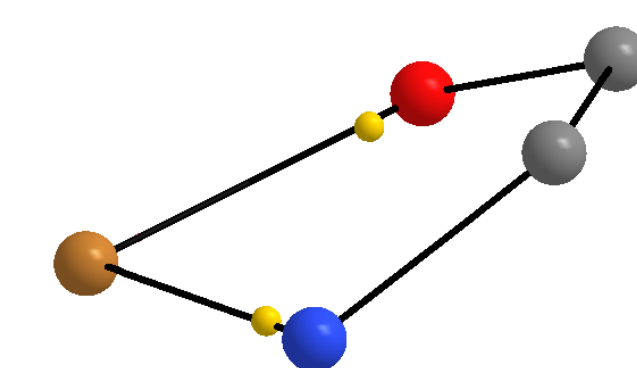


Fig. 3: Concentration CPs from O and N

We classified the contributions from each of the descriptors as positive or negative. A positive contribution means that an increase in the descriptor will tend to increase the formation constant of copper and a negative contribution will decrease the formation constant:

- $\sum \nabla^2 \rho(\mathbf{r})_{cc}(NO)^{\{Fig\ 3\}} \rightarrow$  Positive  $\rightarrow$  Nucleophilic Capacity from Ligands.
- $N(Cu) \rightarrow$  Positive  $\rightarrow$  Electronic population in Cu(II) (gain).
- $\sum \nabla^2 \rho(\mathbf{r})_{cc}(Cu)^{\{Fig\ 1\}} \rightarrow$  Positive  $\rightarrow$  Basicity from Copper(II).
- $\sum \nabla^2 \rho(\mathbf{r})_{cd}(Cu)^{\{Fig\ 1\}} \rightarrow$  Negative  $\rightarrow$  Acidity from Copper(II).

### AGD Models

We find the model shown in Eq (4) for the *AGD* descriptor, where the  $\Delta$  symbol refers to the change between the produced complex and the hexaaquacopper(II) ( $\Delta \equiv \Delta \equiv [CuL_n] - [Cu(H_2O)_6]^{2+}$ ).

$$AGD = -234.113\Delta N_\alpha(Cu) + 239.999\Delta N_\beta(Cu) + 11.653\Delta Q_1(Cu) - 142.693 \quad (4)$$

The direction of the quadrupole component ( $Q_1$ ) is shown in the copper electron density in Fig (4) (Upper part). The direction of the quadrupole component ( $Q_1$ ) in the molecules is shown in Fig (4) (Lower part). The contributions to the *AGD* from the descriptors are:

- $\Delta Q_1(Cu) \rightarrow$  Negative  $\rightarrow$  Shape of density.
- $\Delta N_\alpha(Cu) \rightarrow$  Negative  $\rightarrow \alpha$  Contribution
- $\Delta N_\beta(Cu) \rightarrow$  Positive  $\rightarrow \beta$  Contribution

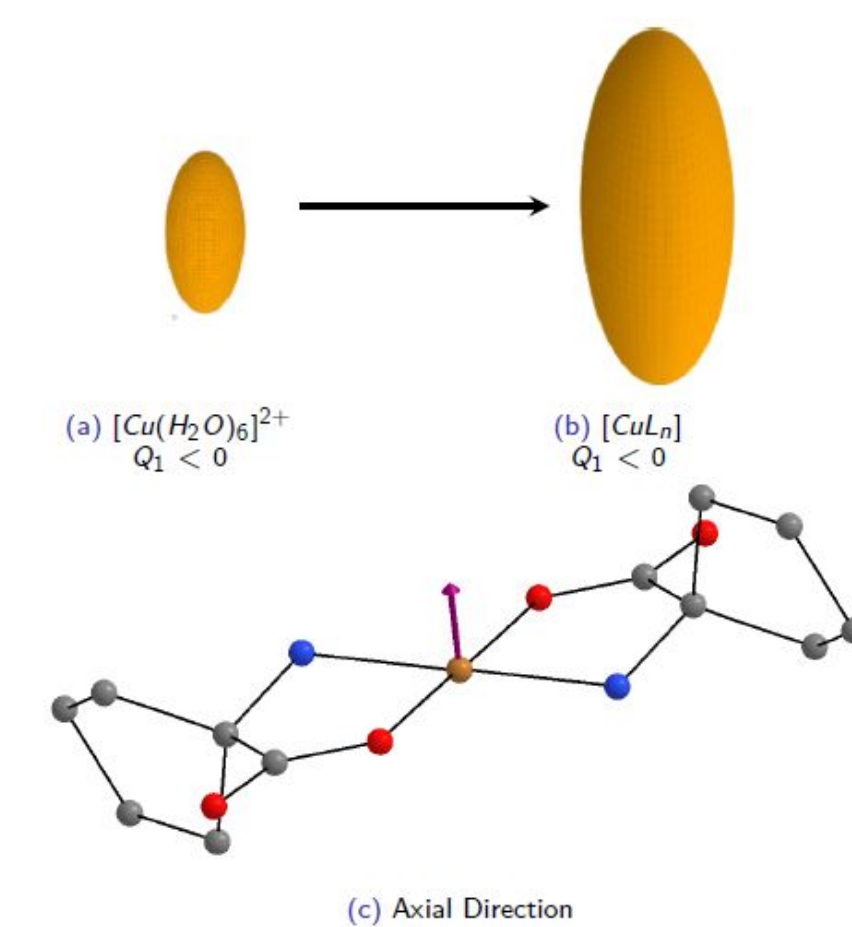


Fig. 4: Quadrupolar Polarizations

Eq	Property	$R^2$	$CV_{R^2}$	F	S.E	Molecules
3	$Log\beta_{exp}$	0.948	0.933	145	0.802	37
4	$AGD$	0.914	0.889	177	0.782	54

Tab. 1: Statistical Parameters of the Models

## Conclusions

- AGD* and  $Log\beta_{exp} \rightarrow$  Possible to create predictive models with the proposed descriptors.
- $Log\beta_{exp} \rightarrow$  Tend to be higher as the bonded atoms increase their nucleophilic capacity and lower as the copper decreases its ability to accept electrons.
- AGD*  $\rightarrow$  Related with polarization terms; change in the form of copper(II) electronic density and gains in the  $\alpha, \beta$  populations.

## References and Acknowledgments

The author thank the PAPIIT project IN202717 from "DGAPA" for the provided Scholarship.

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