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# Core-Level X-Ray Spectroscopies With Relativistic Hamiltonians: The Uranyl Ion Case

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► **To cite this version:**

Wilken Aldair Misael, André Severo Pereira Gomes. Core-Level X-Ray Spectroscopies With Relativistic Hamiltonians: The Uranyl Ion Case. 57th Symposium on Theoretical Chemistry - Universität Würzburg, Sep 2021, Würzburg, Germany. hal-03341123

**HAL Id: hal-03341123**

**<https://hal.science/hal-03341123>**

Submitted on 10 Sep 2021

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## INTRODUCTION

Actinides are broadly used in several fields of science and technology, among other as catalysts in chemical processes [1]. To characterize their behavior one often employs spectroscopic techniques, and among existing methods X-ray spectroscopy is particularly promising in the context of actinides given its great sensitivity and selectivity. With the introduction of advanced X-ray spectroscopy techniques and light sources in recent years, it has recently become possible to investigate different core states of uranium-containing complexes [2].

Analyzing such spectra requires theoretical models capable of describing the electronic structure of actinide species in the ground and excited states [3]. This, in turn requires the use of approaches describing both electron correlation and relativistic effects [4].

## OBJECTIVES

In this work we showcase the use of the Core-Valence-Separated Equation-of-Motion Coupled-Cluster Singles and Doubles (CVS-EOM-CCSD) framework [5] recently implemented in the DIRAC code to investigate the core excited and ionized states of the uranyl ion ( $\text{UO}_2^{2+}$ ) in the gas phase and at the crystalline environment of the dicesium uranyl tetrachloride ( $\text{Cs}_2\text{UO}_2\text{Cl}_4$ ) using different models (Figure 1). For the latter, we combine the CVS-EOM-CCSD method with the Frozen Density Embedding (FDE) method [6].

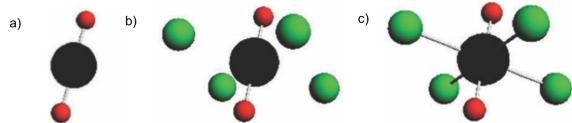
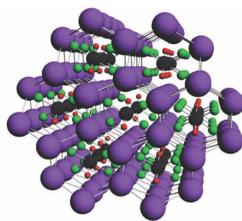


Figure 1 – Models here studied: (Top)  $\text{Cs}_2\text{UO}_2\text{Cl}_4$  crystal. (Bottom) (a)  $\text{UO}_2^{2+}$  ion, (b)  $\text{UO}_2^{2+}$  ion in four chloride potential and (c)  $[\text{UO}_2\text{Cl}_4]^{2-}$  ion, respectively. Adapted from [6].

## THE RELATIVISTIC HAMILTONIAN

Relativistic effects (such as orbital contraction and spin-orbit coupling) are introduced through the choice of Hamiltonian. In the clamped nuclei approximation, the molecular Hamiltonian can be written in terms of the one- ( $\hat{h}_i$ ) and two-electron ( $\hat{g}_{ij}$ ) operators [7]:

$$H = \sum_i \hat{h}_i(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}_{ij}(i,j) + V_{NN} \quad (1.1)$$

and we introduce the coupling between particles and fields through the principle of minimal electromagnetic coupling:

$$\boldsymbol{\pi} \rightarrow \boldsymbol{p} - q\boldsymbol{A} \quad ; \quad E \rightarrow E - q\phi \quad (1.2)$$

The equation to be solved is the Dirac equation for an electron in a molecular field:

$$h_D \psi = E^+ \psi \quad (1.3)$$

where:

$$h_D = c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \boldsymbol{\beta}' mc^2 + V_{ext} = \begin{bmatrix} V_{ext} & c(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) \\ c(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) & V_{ext} - 2mc^2 \end{bmatrix} \quad (1.4)$$

Regarding the two electron part of Eq.(1.1), we have:

$$\hat{g}_{ij} = \underbrace{\hat{g}_{ij}^{Coulomb} + \hat{g}_{ij}^{Gaunt} + \hat{g}_{ij}^{Gauge}}_{\hat{g}_{ij}^{Breit}} = \frac{e^2}{r_{12}} - \frac{e c \alpha_1 \cdot e c \alpha_2}{c^2 r_{12}} - \frac{(e c \alpha_1 \cdot \nabla_1)(e c \alpha_2 \cdot \nabla_2) r_{12}}{2c^2} \quad (1.5)$$

## CVS-EOM-CCSD

In Coupled Cluster theory level (CC) the problem to be solved involve the similarity-transformed Hamiltonian and an exponential parametrization of a reference wave function (e.g. Hartree-Fock) [5]:

$$\hat{H} |\psi_{HF}\rangle = E |\psi_{HF}\rangle \quad ; \quad \hat{H} = e^{-\hat{T}} H e^{\hat{T}} \quad (2.1)$$

In Equation-of-Motion (EOM) theory level, the right-side eigenvalues can be obtained by means of a linear parametrization of the wave function through the excitation operator  $\hat{R}$  :

$$\hat{H} |R_\mu\rangle = E_\mu |R_\mu\rangle \quad ; \quad |R_\mu\rangle = \hat{R}_\mu |\psi_{HF}\rangle \quad (2.2)$$

Core transitions can be easily accessed by means of the Core-Valence Separation scheme (CVS), in which the following eigenvalue equation is solved in order to obtain the energy of target states [5]:

$$P^{CVS} (\hat{H} P^{CVS} |R_\mu\rangle) = E_\mu P^{CVS} |R_\mu\rangle \quad (2.3)$$

## ELECTRONIC EMBEDDING

Environment effects can be incorporated into calculations by means of Frozen Density Embedding (FDE) theory [6].

In density-functional embedding theory the total density of a system can be decomposed as the density from the active system ( $\rho_I$ ) and the density of the environment around it [6], as it can be seen in Figure 3. Within this framework the electronic density, the total energy of the system and the embedding potential are written as:

$$\rho(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r}) \quad (3.1)$$

$$E_{tot} = E[\rho_I(\mathbf{r}), \rho_{II}(\mathbf{r})] = E_I[\rho_I(\mathbf{r})] + E_{II}[\rho_{II}(\mathbf{r})] + E_{int}[\rho_I(\mathbf{r}), \rho_{II}(\mathbf{r})] \quad (3.2)$$

$$V_{emb}^I = \frac{\delta E_{int}[\rho]}{\delta \rho_I(\mathbf{r})} \quad (3.2)$$

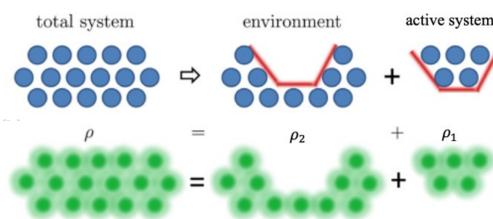


Figure 3 – Schematic view of density-functional embedding theory. Adapted from [11]

In order to investigate the extent of relativistic effects regarding the interaction of X-rays with the bare uranyl ion we have tested the 2- and 4-component Dirac-Coulomb Hamiltonians (respectively  ${}^2\text{DC}^M$  and  ${}^4\text{DC}$ ) and also the eXact-2-Component decoupling scheme in the Atomic Mean Field scheme (X2C-AMFI) in EOM-IP-CCSD calculations. We also have investigated the shifts in orbital energies when the small time integrals (SS|SS) are included in the calculations, or the Gaunt ( ${}^2\text{DCG}^M$ ).

Here we also report our results for a WTF-in-DFT calculation, in which we have used the SAOP+PBE embedding potential obtained in our previous work [6] to study the interaction of the uranyl ion in an four chloride embedding potential at the SCF level in which the 2-component Hamiltonian ( ${}^2\text{DCG}^M$ ) was used (Table 2).

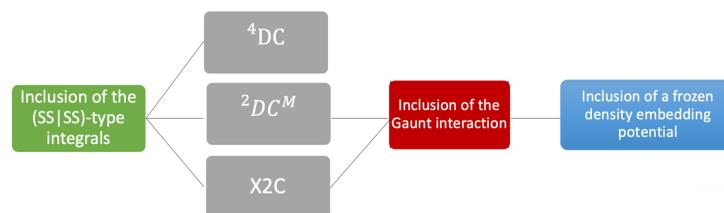


Figure 4 – Scheme from our CVS-EOM-IP-CCSD calculations.

## PHOTOIONIZATION RESULTS

In Figure 4 we show difference between EOM-IP-CCSD calculations at the U  $L_3$ -,  $M_4$ -edges and O K-edge at different Hamiltonians with a 4-component calculation. Table 1 shows our EOM-IP-CCSD at U  $L_3$ -edge calculation and the ones obtained by means of 4-component  $\Delta\text{MP2}$  calculations with the use of dyall.v3z basis set [8]. Table 2 our results to orbital energies at  ${}^2\text{DCG}^M/v2z$  to three different models. Table 3 our results to EOM-IP-CCSD calculations at the  ${}^2\text{DCG}^M/v2z$  theory level.

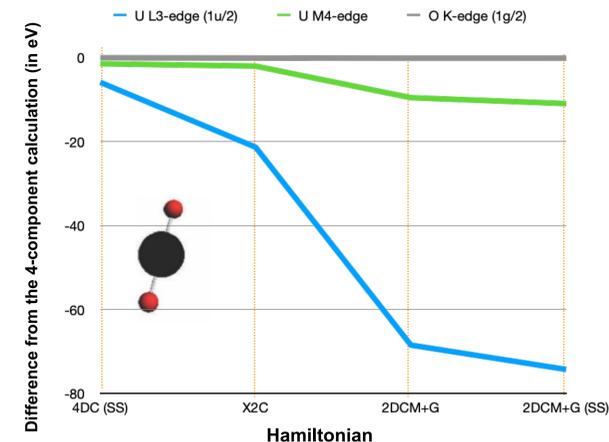


Figure 4 – Results from EOM-IP-CCSD calculations to the bare uranyl ion.

Table 1 – Theoretical values for the U  $L_3$ -edge ionization energy (in eV) for the bare uranyl ion.

	$L_3$ -edge
${}^2\text{DCG}^M$ (SS SS)	17184.3
$\Delta\text{MP2}$ [8]	17251.82

Table 2 - Ionization energies (in eV) for the different models here investigated at the  ${}^2\text{DCG}^M/v2z$  theory level using Koopmans'

	U $L_3$ -edge	O K-edge
$\text{UO}_2^{2+}$ (a)	17254.3	574.6
$\text{UO}_2^{2+}$ in 4 Cl <sup>-</sup> potential [6] (b)	17238.6	558.4
$[\text{UO}_2\text{Cl}_4]^{2-}$ (c)	17232.0	552.5
Experimental	17166.3 [9]	535.4 [10]

Table 3 - Ionization energies (in eV) for the different models here investigated at the  ${}^2\text{DCG}^M/v2z$  theory level using CVS-EOM-IP-CCSD

	U $M_4$ -edge	Cl K-edge	O K-edge
$\text{UO}_2^{2+}$ (a)	3762	-	555.5
$[\text{UO}_2\text{Cl}_4]^{2-}$ (c)	3739	2825.7	533.0
Experimental	3728 [9]	2822.4 [9]	535.4 [10]

## CONCLUSIONS

We have obtained that the use of the  ${}^2\text{DCG}^M$  Hamiltonian provided ionization energies close to the experimental values principally when one employs different methods to describe the interaction of the uranyl ion with equatorial ligands.

Thus, we aim to extend our calculations to other edges and continue to explore different models and other actinides-containing systems.

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