



# Relativistic Equation-of-Motion Coupled-Cluster Calculations at the Uranium L-edge

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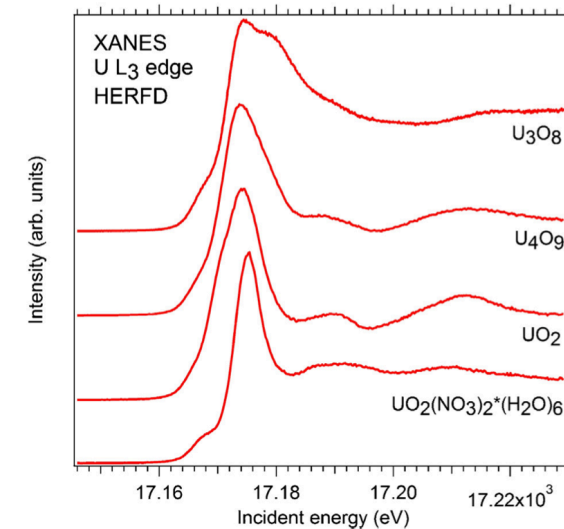
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# Actinides Spectroscopy

- Actinide-containing compounds are broadly used in several fields of science and technology, among others as catalysts in chemical processes and radionucleotides in general research, and also can be encountered as radionuclides in nuclear power plants [1].
- To characterize the nature of the lowest unoccupied states in these systems it is often employed spectroscopy techniques, such as the X-ray absorption near edge structure (XANES) in the hard X-rays range (**Figure 1**).
- One may justify that the use of these high photon energy spectroscopies rises from their great sensitivity and selectivity due to the localized character of these core transitions, allowing the acquisition of information about transitions whose final states involve *d* and *f* orbitals [2].

89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.04	91 <b>Pa</b> Protactinium 231.04	92 <b>U</b> Uranium 238.03	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (266)
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**Figure 1** – (Left) RIXS map at the U L<sub>3</sub> absorption edge of UO<sub>2</sub>. (Right) XANES spectra at the U L<sub>3</sub> absorption edge of different uranium-containing compounds.

Extracted from DOI: 10.1016/j.elspec.2014.01.016 .

[1] Roger M Pallares and Rebecca J Abergel. Nanoscale 12.3 (2020), pp. 1339–1348.

[2] K.O. Kvashnina, F.M.F. de Groot. Journal of Electron Spectroscopy and Related Phenomena 194 (2014) 88–93

# The Relativistic Hamiltonian

The theoretical simulation of the spectra of actinides-containing species is not straightforward, as these species exhibit significant contributions from relativistic and QED effects [3],[4].

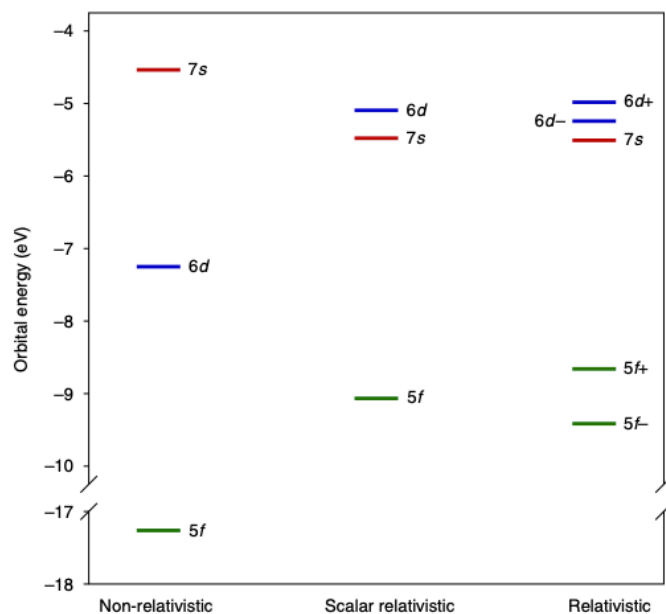


Figure 2 – Effect of relativistic effects in the energy levels of atomic uranium.  
Extracted from DOI: 10.1038/s41557-018-0158-9

These effects can be studied by means of the solution of the Dirac's equation. In Dirac's formalism, the eigenvalue problem to be solved for an electron moving in the electromagnetic field of a set of a nuclei is:

$$h_D \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \begin{pmatrix} V_{ext} & c^2 \\ c(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) & V_{ext} - c^2 \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} E$$

where  $\psi^L$  and  $\psi^S$ , the large and small components of the wave function appears. To reduce computational cost, these components can be decoupled by means of approximated or exact schemes. Regarding molecules, 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:

$$\hat{H} = \sum_i \hat{h}_i + \frac{1}{2} \sum_{i \neq j} \hat{g}_{ij}$$

$$\hat{h}_i \equiv \hat{h}_D(i) = c\boldsymbol{\alpha} \cdot \mathbf{p}(i) + \boldsymbol{\beta}'mc^2 + v_{nuc}$$

$$\hat{g}_{ij} = \hat{g}_{ij}^{Coulomb} + \underbrace{\hat{g}_{ij}^{Gaunt} + \hat{g}_{ij}^{Gauge}}_{\hat{g}_{ij}^{Breit}}$$

[3] Tronde Saue. Relativistic Hamiltonians for chemistry: A primer. ChemPhysChem, v. 12, n. 17, p. 3077-3094, 2011.

[4] Wenzhan Liu. Essentials of relativistic quantum chemistry. In: The Journal of chemical physics, v. 152, n. 18, p. 180901, 2020.



# Equation-of-Motion Coupled-Cluster within the Core-Valence Framework (CVS-EOM-CC)

In this work, we have employed the Equation-of-Motion Coupled-Cluster method truncated at the level of single and doubles excitations (EOM-CCSD).

In the Coupled Cluster theory level, it is assumed the following exponential ansatz for the eigenfunctions of the ground state [5]:

$$|\psi_{CC}\rangle = e^{\hat{T}}|\phi_0\rangle; \hat{T} = \sum_{\mu} t_{\mu}\hat{t}_{\mu}$$

where  $\phi_0$  is the reference wave function and  $\hat{T}$  the cluster operator – defined to a  $\mu$ -excitation manifold.

In this approach the evaluation of excited, attached and ionized states is made by means of the diagonalization of the similarity-transformed Hamiltonian  $\hat{H} \equiv e^{-\hat{T}}\hat{H}e^{\hat{T}}$ .

In the Equation-of-Motion theory level, the right-side eigenvalue can be obtained by means of a linear parametrization of the reference state through the  $\hat{R}$  operator:

$$\hat{H}|R\rangle = E|R\rangle; \quad |\psi\rangle = e^{\hat{T}}\hat{R}|\psi\rangle$$

The form of this operator define the nature of the states to be studied. For excited states:

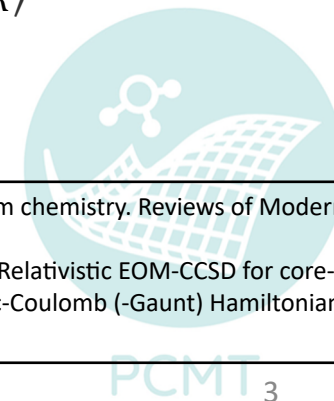
$$\hat{R}^{EE} = r_0 + \sum_{ia} r_i^a \{a_a^\dagger a_i\} + \sum_{i>j, a>b} r_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\} + \dots$$

Core transitions can be easily accessed by means of the Core-Valence Separation scheme[6], in which by means of the definition of a projector of one of the EOM-CC operators (as the right-side one), the following eigenvalue equation is solved in order to obtain the energy of target states:

$$P^{CVS} \left( \hat{H} P^{CVS} |R\rangle \right) = E P^{CVS} |R\rangle$$

[5] Bartlett, R. J., & Musiał, M. (2007). Coupled-cluster theory in quantum chemistry. *Reviews of Modern Physics*, 79(1), 291.

[6] Halbert, L., Vidal, M.L., Shee, A., Coriani, S. and Gomes, A.S.P., 2020. Relativistic EOM-CCSD for core-excited and core-ionized state energies based on the 4-component Dirac-Coulomb (-Gaunt) Hamiltonian. arXiv preprint arXiv:2011.08549.



# Methodology

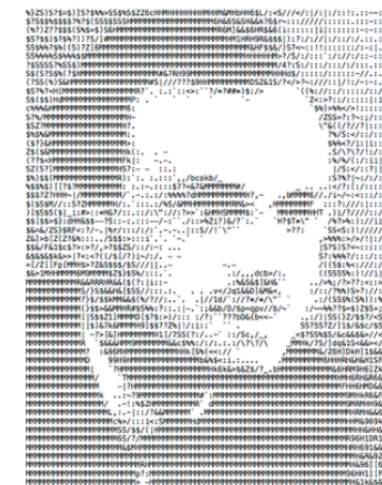
We performed the calculation of the excitation energies for the first transitions at the uranium  $L_1$ ,  $L_2$  and  $L_3$  edges ( **$2s \rightarrow 6d$** ,  **$2p_{1/2} \rightarrow 6d$**  and  **$2p_{3/2} \rightarrow 5d$** , respectively) in the bare uranyl ion ( $\text{UO}_2^{2+}$ ) using the CVS-EE-EOM-CCSD framework, testing different approximations for the one- and two-electron operators and different types of spinors [3],[4]:

- 1) 4-component calculations, with or without the inclusion of the small component (or  $\langle SS|SS \rangle$  type) integrals;
- 2) 2-component calculations employing the eXact 2-component decoupling scheme (X2C) for the one-electron Dirac Hamiltonian.
- 3) In the 2-component calculations, the block diagonalization scheme (from 4-component to 2-component) after the SCF convergence scheme, also known as the Molecular Mean Field (MMF) approach, was also tested.

[7] Saue, T., Bast, R., Gomes, A.S.P., Jensen, H.J.A., Visscher, L., Aucar, I.A., Di Remigio, R., Dyall, K.G., Eliav, E., Fasshauer, E. and Fleig, T., 2020. The DIRAC code for relativistic molecular calculations. The Journal of chemical physics, 152(20), p.204104.

4) Also for the 2-component calculations, it was tested the Inclusion of spin other orbit interaction (SOO) by means of the inclusion of the Gaunt operator.

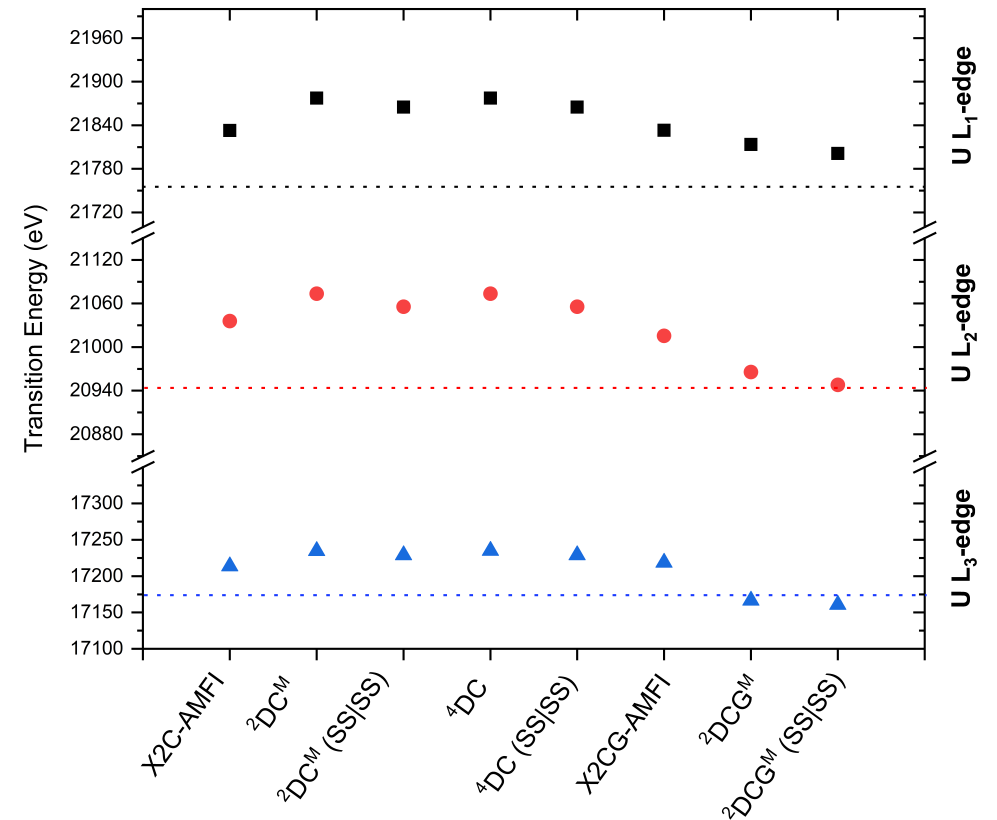
All calculations were performed in the DIRAC electronic structure code [7], employing Dyal's basis sets of double-zeta quality (dyall.v2z) for all species. Also, all occupied and virtual spinors were computed for the correlation treatment.



<http://diracprogram.org>  
@DIRACprogram

# Results and some remarks

- The similarity between the results obtained by the  $^4\text{DC}$  and  $^2\text{DC}^{\text{M}}$  are in agreement with our previous studies [6];
- Due the spin-orbit coupling present in the  $L_{2,3}$ -edges, the inclusion of the Gaunt interaction is appreciated for all the Hamiltonians here used;
- The  $^2\text{DCG}^{\text{M}}$  Hamiltonian is the one that generates the smallest deviations to experiment. However, as observed for the  $L_3$ -edge results, the use of this Hamiltonian can underestimate the experimental value.
- All of our results for the  $L_3$ -edge have small deviation from the experiment when compared with the with STEX calculations reported by South et al. (17238 eV)[8].



**Figure 3** – Results for the CVS-EE-EOM-CCSD calculations at the U L1, L2 and L3-edge. The blue dotted line refers to [9], the red and the black dotted line to [10].

[8] South, C., Shee, A., Mukherjee, D., Wilson, A.K. and Saue, T., 2016. 4-Component relativistic calculations of L 3 ionization and excitations for the isoelectronic species UO 2 2+, OUN+ and UN 2. *Physical Chemistry Chemical Physics*, 18(31), pp.21010-21023.

[9] Vitova, T., Green, J.C., Denning, R.G., Löble, M., Kvashnina, K., Kas, J.J., Jorissen, K., Rehr, J.J., Malcherek, T. and Denecke, M.A., 2015. Polarization dependent high energy resolution X-ray absorption study of dicesium uranyl tetrachloride. *Inorganic chemistry*, 54(1), pp.174-182.

[10] Deslattes, R.D., Kessler Jr, E.G., Indelicato, P., De Billy, L., Lindroth, E. and Anton, J., 2003. X-ray transition energies: new approach to a comprehensive evaluation. *Reviews of Modern Physics*, 75(1), p.35.

# Conclusions and Some Perspectives

In this work we have carried out the calculation of the excitation energies at the L-edge of uranium using the CVS-EE-EOM-CCSD framework varying the Hamiltonian and the spinors used in these calculations.

We have obtained that the using the Molecular Mean Field approach with the gaunt operator and the use of the small component integrals it was possible to achieve excitation energies near the experimental values.

We will to extend our studies to other actinide-containing species and also:

- Extend our calculations to other edges of experimental interest.
- Calculations of ionization energies within the CVS-EOM-CC-IP framework;
- Calculations considering environmental effects by means of Frozen Density Embedding (FDE) calculations in excitation and ionization energies.
- Include energy corrections to account the full (zero-frequency) Breit interaction and QED effects.

## Acknowledgments

