NOVA SCHOOL OF SCIENCE & TECHNOLOGY

DEPARTMENT OF PHYSICS

GONÇALO GARCÊS SOBREIRA RODRIGUES BAPTISTA

BSc in Physics Engineering

X-RAY RESONANT RAMAN SCATTERING

SPECTRA SIMULATION FROM FIRST PRINCIPLES FOR COPPER BELLOW IONIZATION THRESHOLD USING HIGH-PERFORMANCE COMPUTING

MASTER IN PHYSICS ENGINEERING

NOVA University Lisbon

Draft: *February 15, 2023*

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Advisers: Jorge Felizardo Machado
Auxiliary Professor, NOVA University Lisbon
Mauro António Guerra
Auxiliary Professor, NOVA University Lisbon

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Abstract

The work performed on this thesis comes as part of the effort to further understand the highly convoluted structure present on Copper's x-ray emission spectra, where, as with many other transition metals, a skewness can be observed on the $K_{\alpha_{1,2}}$, K_{β} and L transition lines. These line originate due to the radiative relaxation of the atom's electronic structure post-ionization of inner shell electrons. However, it is possible that the observed skewness is due to copper's satellite states' transitions.

Throughout this thesis, a study will be performed for the satellite states formed by the excitation of the inner-shell electron, where the ionization process did not occur.

Multiple atomic structure calculations will be performed using the *ab initio* state of the art Multiconfiguration Dirac-Fock General Matrix of Elements (*MCDFGME*) code for different excited states configurations (from an electron in the 4*s* orbital up to n=??).

The obtained results will then be used in the analysis of experimental data obtained from a High-Precision Double Crystal Spectrometer (DCS), located in Paris, in a synchrotron line.

Due to the complexity of the calculations, the process can become quite hefty in terms of computational power and time. Therefore, further similar and more complex studies will be performed by implementing and running a script in the *Oblivion* supercomputer located at the University of Évora.

Keywords: Excited State, Diagram Lines, *MCDFGME*, DCS, High Performance Computing

Resumo

Independentemente da língua em que a dissertação está escrita, geralmente esta contém pelo menos dois resumos: um resumo na mesma língua do texto principal e outro resumo numa outra língua.

A ordem dos resumos varia de acordo com a escola. O comportamento padrão para o template NOVAthesis LaTeX (novathesis) é ter em primeiro lugar o resumo *na mesma língua do texto principal* e depois o resumo *na outra língua*. Por exemplo, se a dissertação for escrita em português, a ordem dos resumos será primeiro em português e depois em inglês, seguido do texto principal em português. Se a dissertação for escrita em inglês, a ordem dos resumos será primeiro em inglês e depois em português, seguido do texto principal em inglês. O template novathesis (LaTeX) irá ordenar automaticamente os resumos por uma ordem apropriada. No entanto, esta ordem pode ser personalizada adicionando

```
\abstractorder(<MAIN_LANG>):={<LANG_1>,...,<LANG_N>}
```

ao ficheiro `5_packages.tex`. Por exemplo, para um documento escrito em Alemão com resumos em Alemão, Inglês e Italiano (por esta ordem), pode usar-se:

```
\abstractorder(de):={de,en,it}
```

Relativamente ao seu conteúdo, os resumos não devem ultrapassar uma página e frequentemente tentam responder às seguintes questões (é imprescindível a adaptação às práticas habituais da sua área científica):

1. Qual é o problema?
2. Porque é que é um problema interessante/desafiante?
3. Qual é a proposta de abordagem/solução?
4. Quais são as consequências/resultados da solução proposta?

Palavras-chave: Primeira palavra-chave, Outra palavra-chave, Mais uma palavra-chave, A última palavra-chave

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Acronyms

MCDFGME Multiconfiguration Dirac-Fock General Matrix of Elements *(p. ii)*

DCS Double Crystal Spectrometer *(p. ii)*

novathesis NOVAthesis LaTeX *(p. iii)*

Chapter 1

Introduction

1.1 Theoretical Introduction

1.1.1 Characteristic x-rays

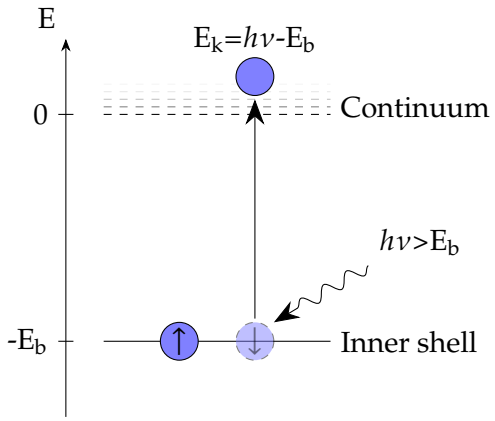

Figure 1.1: Photoionization

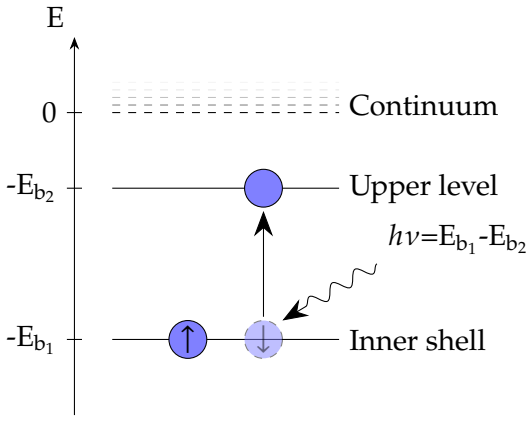

Figure 1.2: Resonant Photoexcitation

1.2 Atomic Structure Calculations

When studying a system composed of multiple charged bodies, one must consider all the existing interactions. Whilst there are known solutions for the 2-bodies Hydrogenoid systems, with the presence of more non spatially-bound particles (for example an electron, while using the Born-Oppenheimer approximation where the nuclei are considered at rest at a fixed position) there is just no analytic solution for the Schrödinger Equation. That way, there was a need for the development of numerical solutions able to solve this problem.

1.2.1 The non-relativistic Hamiltonian

The first approach used in order to solve the many-bodies problem used a non-relativistic consideration. This way, the used Hamiltonian consisted on simply the sum of the system's non-relativistic momentum-related energies and the Coulomb interactions between bodies, while still considering the Born-Oppenheimer approximation.

Essentially, and in atomic units:

$$H = \underbrace{\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}}_{\text{Individual Hamiltonian}} + \underbrace{\sum_{i<j}^{j} \frac{1}{r_{ij}}}_{\text{Pair repulsion}} \tag{1.1}$$

1.2.1.1 The Hartree-Fock Method

Hartree developed an iterative method, further enhanced by Fock and Slater,

1.2.1.2 Radiative transition type

One photon transition rates:

Non-relativistic: $dA_{10} = \frac{e^2\omega}{2\pi\hbar c}\left|\left\langle 0\left|\boldsymbol{p}\boldsymbol{\epsilon}^* \cdot \frac{1}{m_e c}\right|1\right\rangle\right|^2$

1.2.2 The Dirac Equation

It is no secret that the Schrödinger equation has some very considerable limitations. The fact that it does not account for the existence of the electron's spin and the lack of consideration of relativistic effects are some of the most impactful setbacks.

That way, a new equation was developed by Paul Dirac, in 1928[1], one taking into account now not the classical 3 dimensional space components, but the relativistic four components (1 time-like and 3 space-like).

Many scientists, such as Klein, Gordon and later Fock, had already conceived a relativistic correction to Schrödinger's equation, more commonly known as the Klein-Gordon equation(1.3), where the free-particle energy makes use of the relativistic momentum-energy relation (1.2), making Schrödinger's equation now also Lorentz-invariant. This

new approach was, however, still faulty, due to only describing spin 0 particles (e.g., some mesons), and making use of a second order derivative in the time-like component.

$$E = \sqrt{c^2p^2 + m^2c^4} \tag{1.2}$$

$$-\hbar^2 \frac{\partial^2}{\partial t^2}\boldsymbol{\Psi} = -c^2\hbar^2\nabla^2 + m^2c^4\boldsymbol{\Psi} \tag{1.3}$$

Dirac took a spin at rewriting the energy-momentum relation, ending up with an equivalent equation(1.4), involving 4×4 matrices, due to the 4 dimensions at play, and incorporating spins into the equation by making use of the now famous Pauli matrices, $\boldsymbol{\sigma}$:

$$E = c\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta mc^2, \quad \boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3) \tag{1.4}$$

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \qquad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{1.5}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1.6}$$

In order to fully comprehend this shift of notation, one should equate the square of the two equations, (1.2) and (1.4), and confirm if logic still stands.

$$c^2p^2 + m^2c^4 = c^2\boldsymbol{\alpha}^2\boldsymbol{p}^2 + 2mc^3\boldsymbol{\alpha} \cdot \boldsymbol{p} \cdot \beta + \beta^2m^2c^4 \tag{1.7}$$

In order for this equation to make sense, the following conditions must be true (which in fact, they are):

$$\begin{cases} c^2p^2 = c^2\boldsymbol{\alpha}^2p^2 & \Leftrightarrow \boldsymbol{\alpha}^2 = 1 \\ 0 = 2mc^3p\boldsymbol{\alpha}\beta & \Leftrightarrow \boldsymbol{\alpha}\beta = 0 \\ m^2c^4 = \beta^2m^2c^4 & \Leftrightarrow \beta^2 = 1 \end{cases} \tag{1.8}$$

1.2.2.1 Breit Interaction

1.2.2.2 Vacuum Polarization

1.2.2.3 Self-Consistency

1.2.2.4 Hartree Method

1.2.2.5 General Matrix of Elements

1.3 State of the Art

1.3.1 MCDF

1.3.2 Copper's characteristic x-rays

1.4 Objective list

1.5 Work Plan

Bibliography

[1] P. A. M. Dirac. "The quantum theory of the electron". In: *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 117 (778 1928-02), pp. 610–624. ISSN: 0950-1207. DOI: 10.1098/rspa.1928.0023 (cit. on p. 2).