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 16, 2023*

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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

```
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```

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

Contents

List of Figures

List of Tables

Acronyms

MCDFGME Multiconfiguration Dirac-Fock General Matrix of Elements *(pp. ii, iv, 6)*

DCS Double Crystal Spectrometer *(p. ii)*

novathesis NOVAthesis LaTeX *(p. iii)*

Chapter 1

Introduction

1.1 Theoretical Introduction

1.1.1 Characteristic x-rays

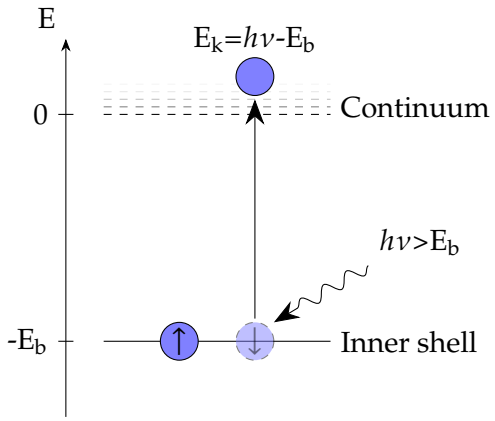

Figure 1.1: Photoionization

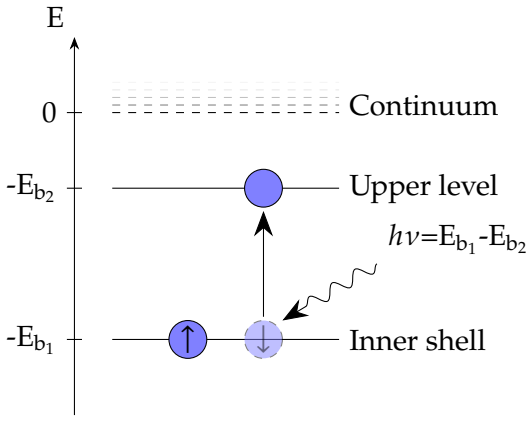

Figure 1.2: Resonant Photoexcitation

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, based on the field self-consistency method.

In this method, while studying a multi-electronic system, such as an atom, each electron's wavefuction is composed as a product of a spacial part, ψ, and one indicating the electron's spin, χ, as to account for Pauli's exclusion principle.

$$u = \psi\chi \tag{1.2}$$

The wavefuction capable of describing the whole system, Ψ, should be somewhat of a product of all the wavefunctions describing each individual electron. However, one must not forget the need for this wavefunction respect the antisymmetry principle, due to the electron's fermionic nature. In order to respect this, Ψ is to be composed of a Slater determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(x_1) & u_2(x_1) & \cdots & u_N(x_1) \\ u_1(x_2) & u_2(x_2) & \cdots & u_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_1(x_N) & u_2(x_N) & \cdots & u_N(x_N) \end{vmatrix} \tag{1.3}$$

It is of high importance that the wavefunctions must form an orthonormal basis. These are to be initialized as trial wavefunctions.

The main goal of this method is to follow the variational principle and to minimize a functional, with the purpose of minimizing the system's energy. Assuming the optimal, yet unknown energy, E_0 (calculated by Operating the Hamiltonian on the optimal wavefunctions), it is natural to assume the used test functions provide a non-minimized solution, with $\langle\Psi|H|\Psi\rangle \geq E_0$.

The computational method consists on starting with the previously mentioned test wavefunctions, using them to calculate Hartree-Fock's potential through the HF equations,

In a very simplified way, the self-consistent Hartree-Fock computational method can be represented by the following block diagram:

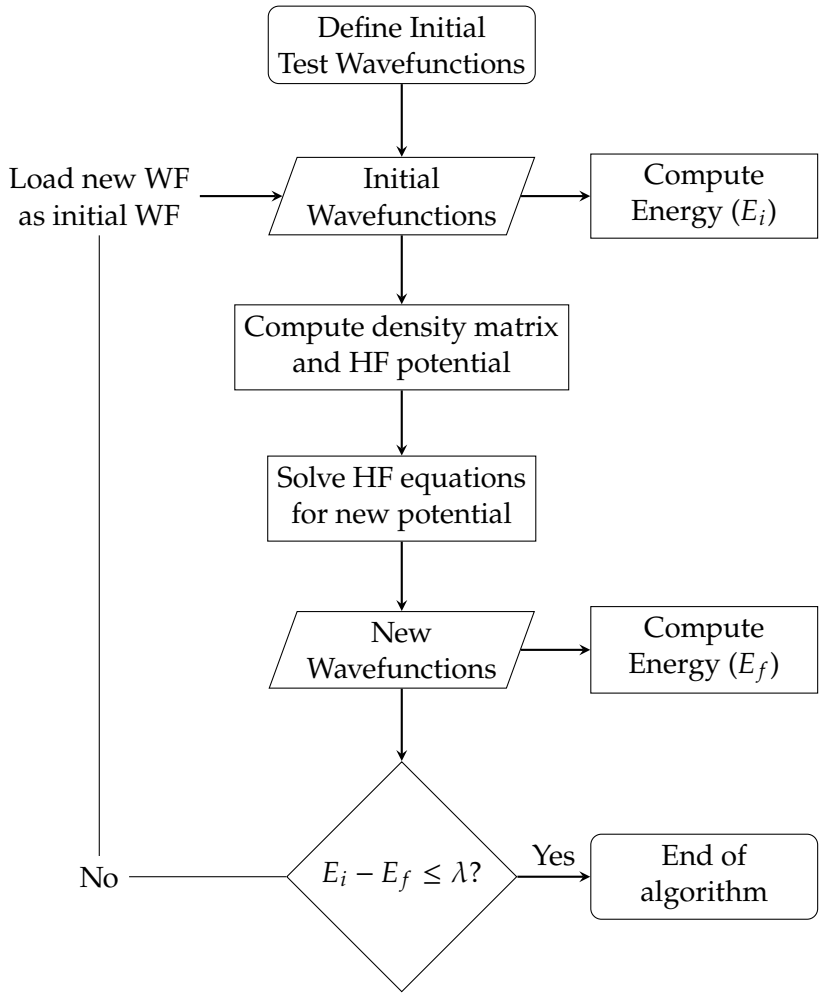

Figure 1.3: Diagram

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[2], 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(1.6), where the free-particle energy makes use of the relativistic momentum-energy relation (1.4), 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.

$$E = \sqrt{c^2\boldsymbol{p}^2 + m^2c^4} \tag{1.4}$$

Which can be derived from:

$$\frac{E^2}{c^2} = \boldsymbol{p}^2 + m^2c^2 \Leftrightarrow \frac{E^2}{c^2} - \boldsymbol{p}^2 = m^2c^2 \Leftrightarrow p^\mu p_\mu = m^2c^2 \tag{1.5}$$

Just as a reminder, since now relativistic effects are being taken into account, the momentum vector is now a 4-vector, composed of one time-like and 3 space-like components: $p^\mu = (p^0.p^1, p^2, p^3) = (p^0, \boldsymbol{p}) = \left(\frac{E}{c}, \boldsymbol{p}\right)$

$$-\hbar^2\frac{\partial^2}{\partial t^2}\boldsymbol{\psi} = -c^2\hbar^2\nabla^2 + m^2c^4\boldsymbol{\psi} \tag{1.6}$$

Dirac took a spin at rewriting the energy-momentum relation, ending up with an equivalent equation(1.7), involving 4×4 matrices, due to the 4 relativistic dimensions at play, and incorporating spins into the equation by making use of the now famous Pauli matrices, $\boldsymbol{\sigma}$:

$$E = c\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta mc^2, \quad \boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3) \tag{1.7}$$

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix} \qquad I_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{1.8}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1.9}$$

In order to fully comprehend this shift of notation, one should equate the square of the two equations, (1.4) and (1.7), and confirm if logic still stands.

$$c^2\boldsymbol{p}^2 + m^2c^4 = c^2\boldsymbol{\alpha}^2\boldsymbol{p}^2 + 2mc^3\boldsymbol{\alpha}\cdot\boldsymbol{p}\cdot\beta + \beta^2m^2c^4 \tag{1.10}$$

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

$$\begin{cases} c^2\boldsymbol{p}^2 = c^2\boldsymbol{\alpha}^2p^2 & \Leftrightarrow \boldsymbol{\alpha}^2 = 1 \\ 0 = 2mc^3p\boldsymbol{\alpha}\beta & \Leftrightarrow \boldsymbol{\alpha}\beta = 0 \\ m^2c^4 = \beta^2m^2c^4 & \Leftrightarrow \beta^2 = 1 \end{cases} \tag{1.11}$$

As expected, the eigenfunctions obtained from solving this equation, will now have a 4th time-like component, in addition to the already expected 3 space-like components.

With all the previous considerations taken into account, one can now construct Dirac's free-particle equation(1.12):

$$i\hbar\frac{\partial}{\partial t}\boldsymbol{\psi} = \left(c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2\right)\boldsymbol{\psi} = \begin{pmatrix} mc^2I_2 & -i\hbar c\boldsymbol{\sigma}\cdot\boldsymbol{\nabla} \\ -i\hbar c\boldsymbol{\sigma}\cdot\boldsymbol{\nabla} & -mc^2I_2 \end{pmatrix}\cdot\begin{pmatrix} \psi_1 \\ \vdots \\ \psi_4 \end{pmatrix} \tag{1.12}$$

This equation, however, as previously mentioned above, can only describe a single particle present in a field-free region. In order to account for the existence of a field, such as the electromagnetic field, derived from the four-potential A^μ, composed by the electric scalar potential, $A^0 = \phi$, and the vector potential, $(A^1, A^2, A^3) = \boldsymbol{A}$:

$$p^\mu \rightarrow p^\mu - eA^\mu, \quad A^\mu = \left(\phi, \boldsymbol{A}\right) \tag{1.13}$$

The Hamiltonian can now be rewritten as to account for the presence of the electromagnetic field (1.14). This way it is possible to include, for example, the electron-nucleus Coulomb attraction.

$$H_D = -e\phi + \beta mc^2 + \boldsymbol{\alpha}(c\boldsymbol{p} + e\boldsymbol{A}) \tag{1.14}$$

For a central potential, as is the one generated by the nuclear charge, the 3 space-like components from the four-potential are null, and the time-like component, $\phi = \dfrac{Ze}{r}$. The equation gains now a more recognizable term:

$$H_D = -\frac{e^2Z}{r} + \beta mc^2 + \boldsymbol{\alpha}\cdot\boldsymbol{p}c \tag{1.15}$$

1.2.3 The Dirac-Breit Equation

Once again, when considering a system composed of many bodies, one must consider all the present interactions, namely, the electron-electron repulsion in an atom. Breit, in 1929, had already created a relativistic approach to treat the electron-electron interactions, consisting on a set of equations building upon the classical non-relativistic Hamiltonian from equation (1.1), which can be consulted in appendix 1.5. Breit's equations are able to account for angular momenta couplings and estimate level energy splittings, the change of a particle's apparent mass as a function of velocity, and even include the interaction of an applied external magnetic field.[1]

It is quite obvious Breit's equations introduce a great complexity in the search of the new Hamiltonian's eigenfunctions. However, when trying to include an approximation of Breit's considerations into Dirac's equation, one must add the following operator to the one present in equation (1.15):

$$H_B = \sum_{i>j} \frac{e^2}{r_{ij}} - e^2 \left(\frac{\boldsymbol{\alpha}_i \boldsymbol{\alpha}_j}{r_{ij}} + \frac{(\boldsymbol{\alpha}_i \boldsymbol{\nabla}_i)(\boldsymbol{\alpha}_j \boldsymbol{\nabla}_j) r_{ij}}{2} \right) \tag{1.16}$$

1.2.4 The *MCDFGME* Method

As previously mentioned in section 1.2.1.1, there is a need for a numerical method in order to compute and find the eigenfunctions for a many-body Hamiltonian. While the Hartree-Fock method was able to reasonably solve the non-relativistic problem, now, while considering the Dirac-Breit Hamiltonian from equations (1.15) and (1.16), there is a need for a new method.

Hence, the state of the art *MCDFGME* arises. This self-consistent iterative method, based on the same method present in section 1.2.1.1, is able to solve and find eigenfunctions for a multielectronic system, now taking into account the Dirac-Breit Hamiltonian. Moreover, it is also capable of incorporating electron correlation and many QED effects not yet considered in the relativistic equation, such as the Lamb-shift, vacuum polarization, and the electron's self energy. A brief description of these contributions can be found in appendix ???

EXPLICAR A GENERAL MATRIX OF ELEMENTS.

1.3 State of the Art

1.3.1 Copper's characteristic x-rays

1.3.2 MCDFGME capabilities

1.4 Objective list

1.5 Work Plan

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[2] 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. 4).

Appendix A

The Breit Hamiltonian Equations

Note: This equations are valid for the electrons in an atom.
The free particle energy:

$$H_0 = \sum_i^N \frac{p^2}{2m_e} \tag{A.1}$$

The electron-nucleus Coulomb attraction:

$$H_1 = \sum_i^N -\frac{e^2 Z}{r_i} \tag{A.2}$$

The electron-electron Coulomb repulsion:

$$H_2 = \sum_{i>j} \frac{e^2}{r_{ij}} \tag{A.3}$$

asdkjhdajkhdsajdhjska:

$$H_3 = -\frac{1}{8{m_e}^3 c^2} \sum_i^N p_i^4 \tag{A.4}$$

ACABAR O RESTO