Gonçalo Garcês S.R. Baptista
Bsc. in Physics Engineering

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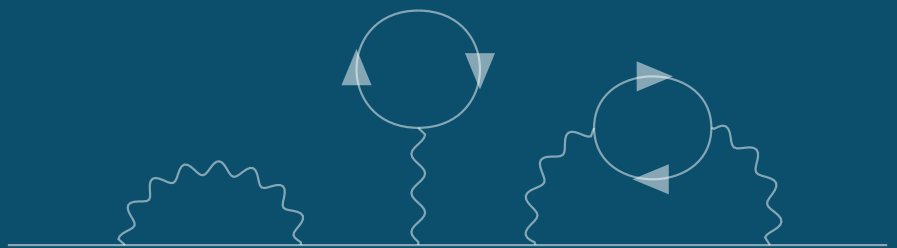
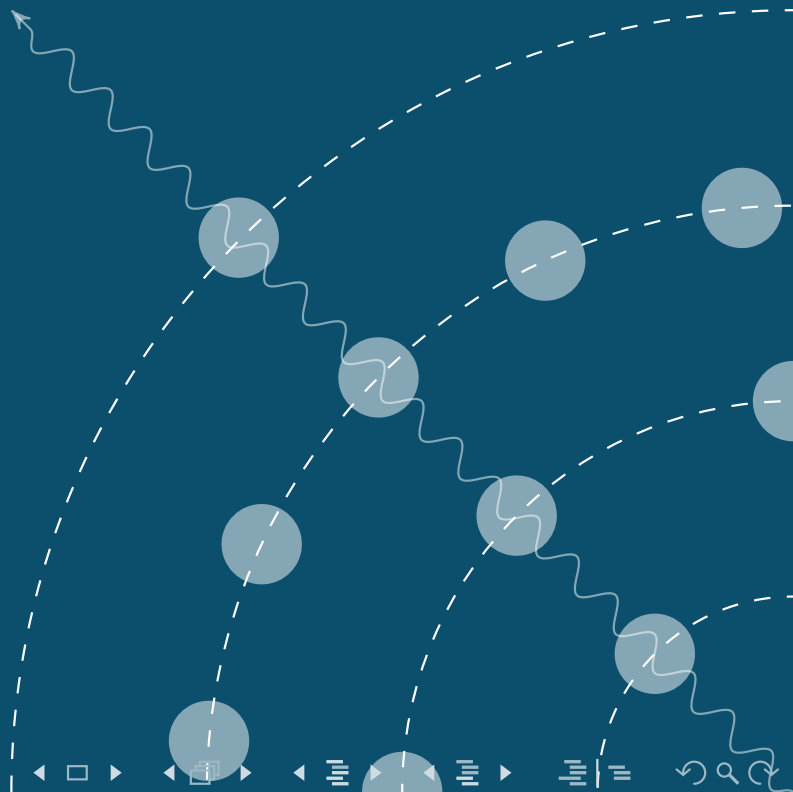
Rapporteur: Prof. Jorge Sampaio
Advisor: Prof. Mauro Guerra
Co-Advisor: Prof. Jorge Machado

NOVA School of Science and Technology

X-ray Resonant Raman Scattering

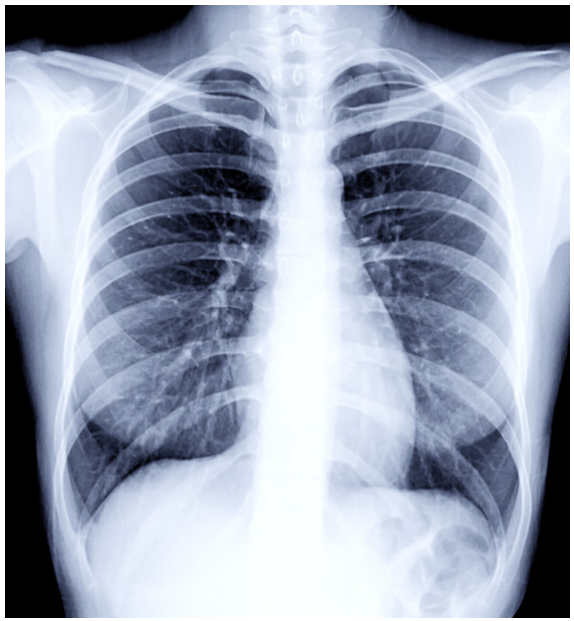
Spectra simulation from first principles for Copper below the ionization threshold using high-performance computing





Overview

X-ray applications



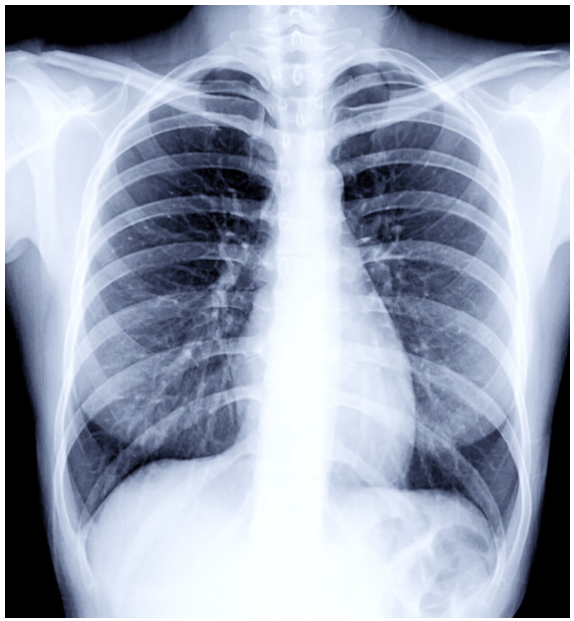
(a) Imaging purposes

(b) Sample quantification

(c) Fundamental parameters

Figure: Application examples of x-ray radiation

X-ray applications



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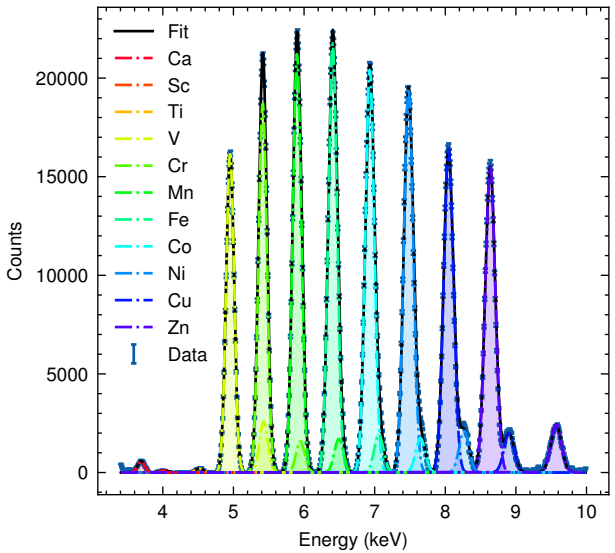

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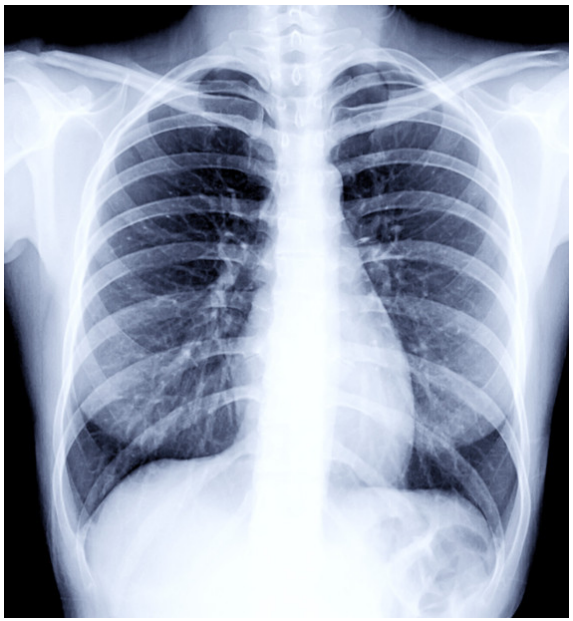

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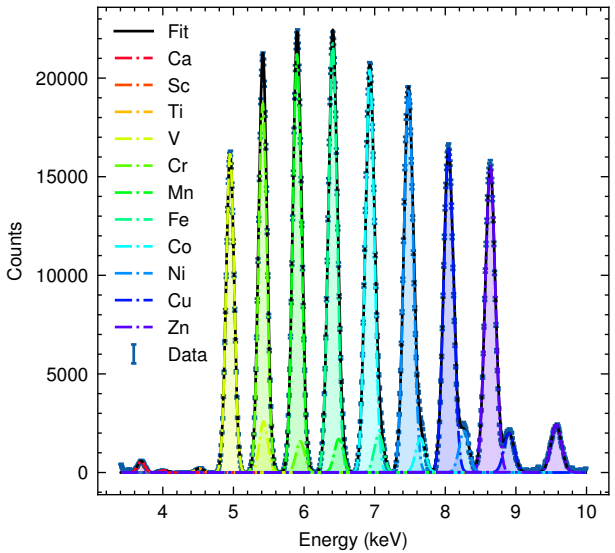

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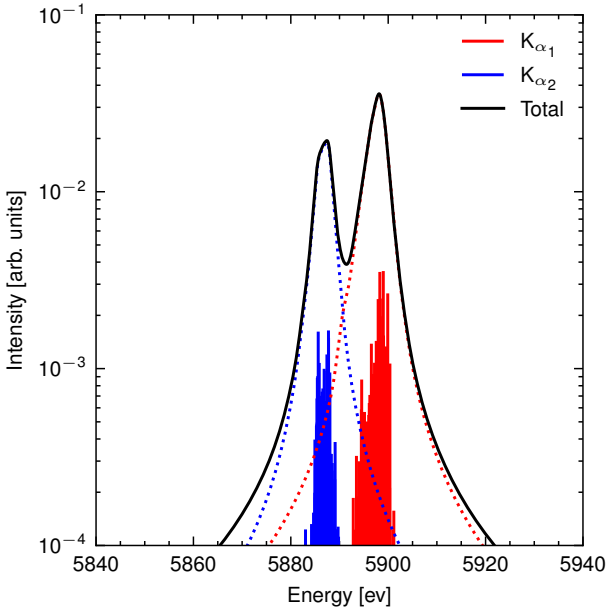

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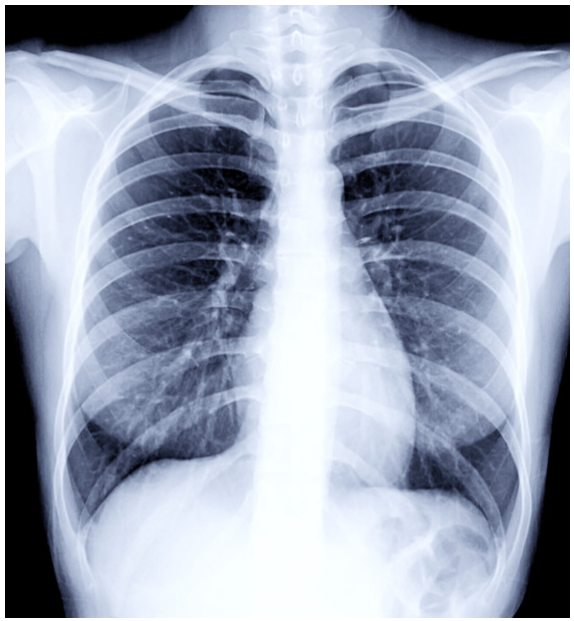

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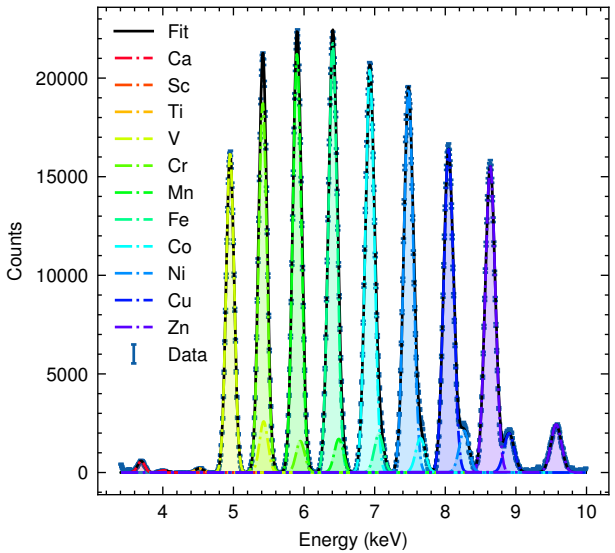

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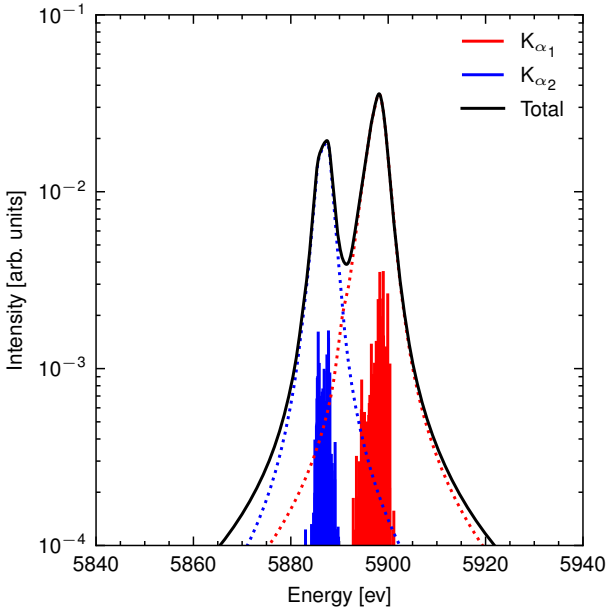

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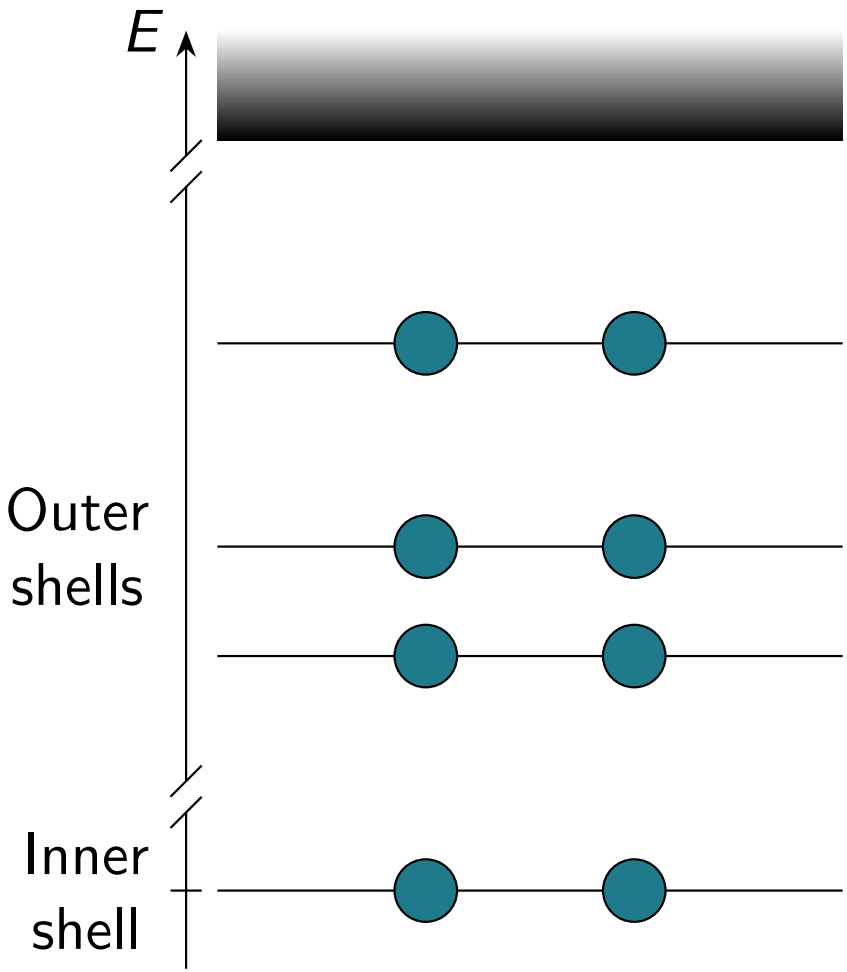
Vacancy generation and relaxation processes



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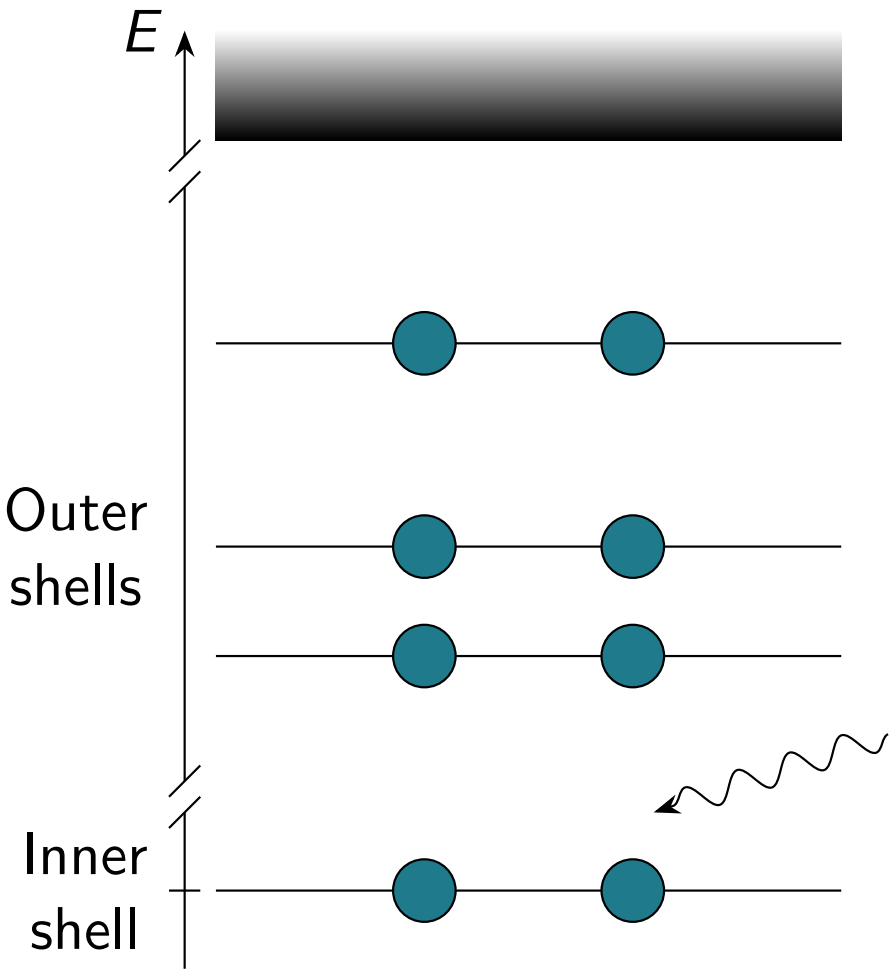

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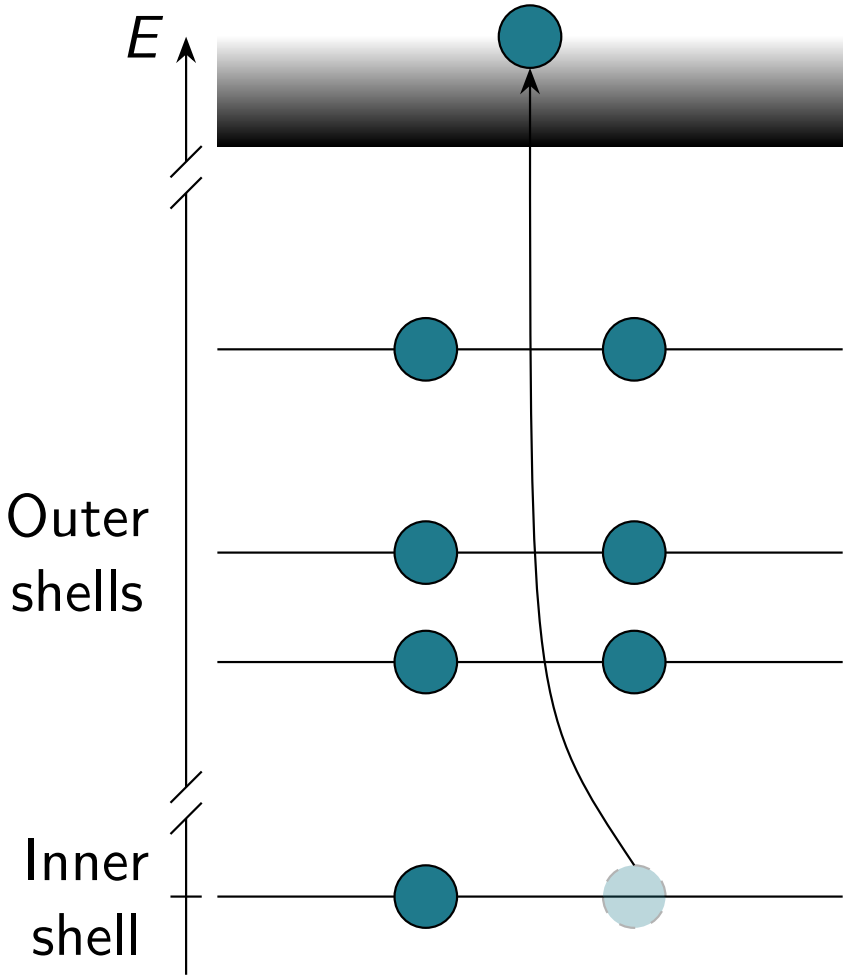

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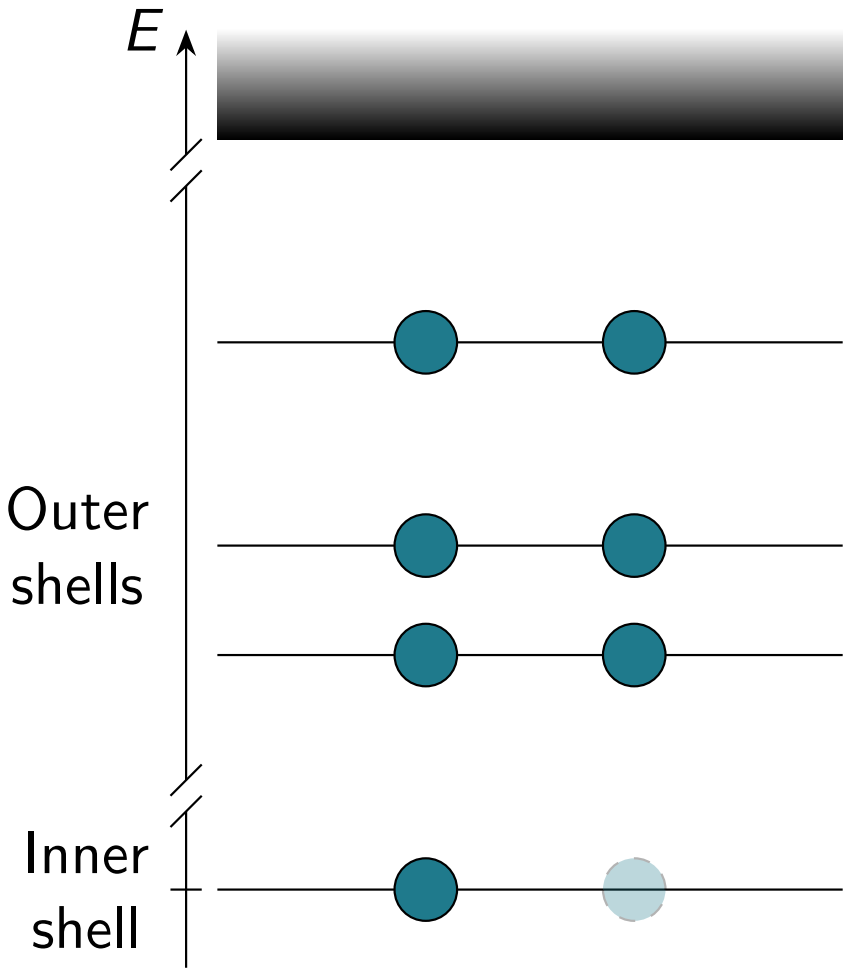

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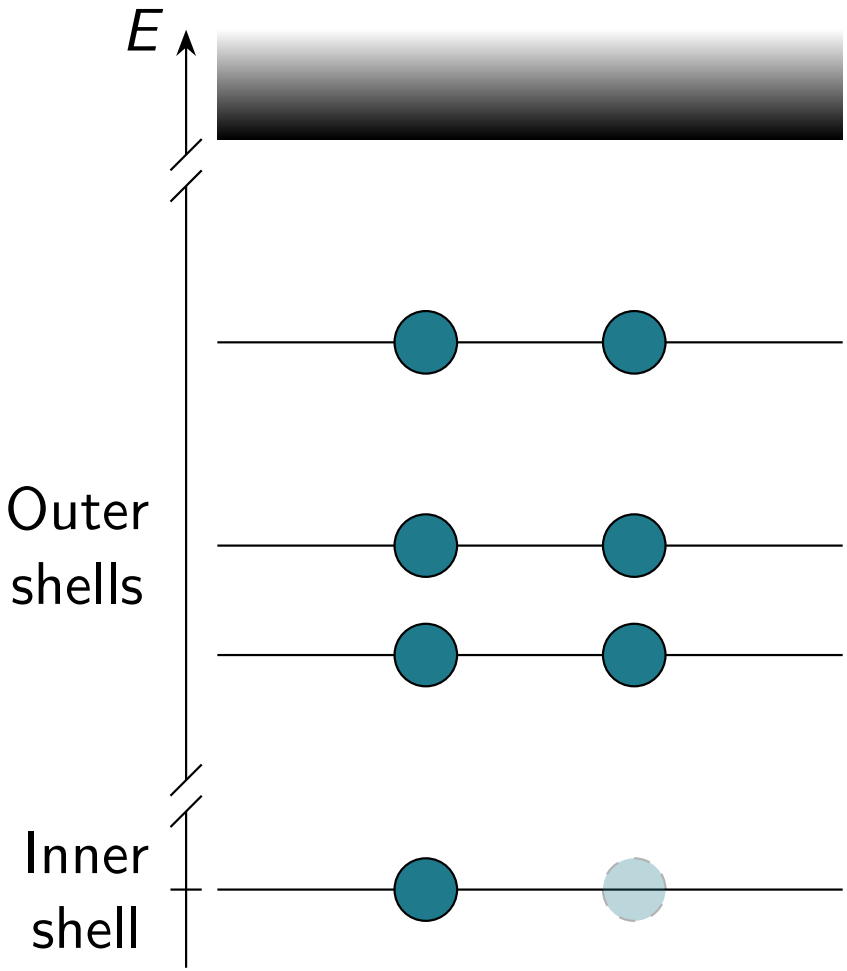

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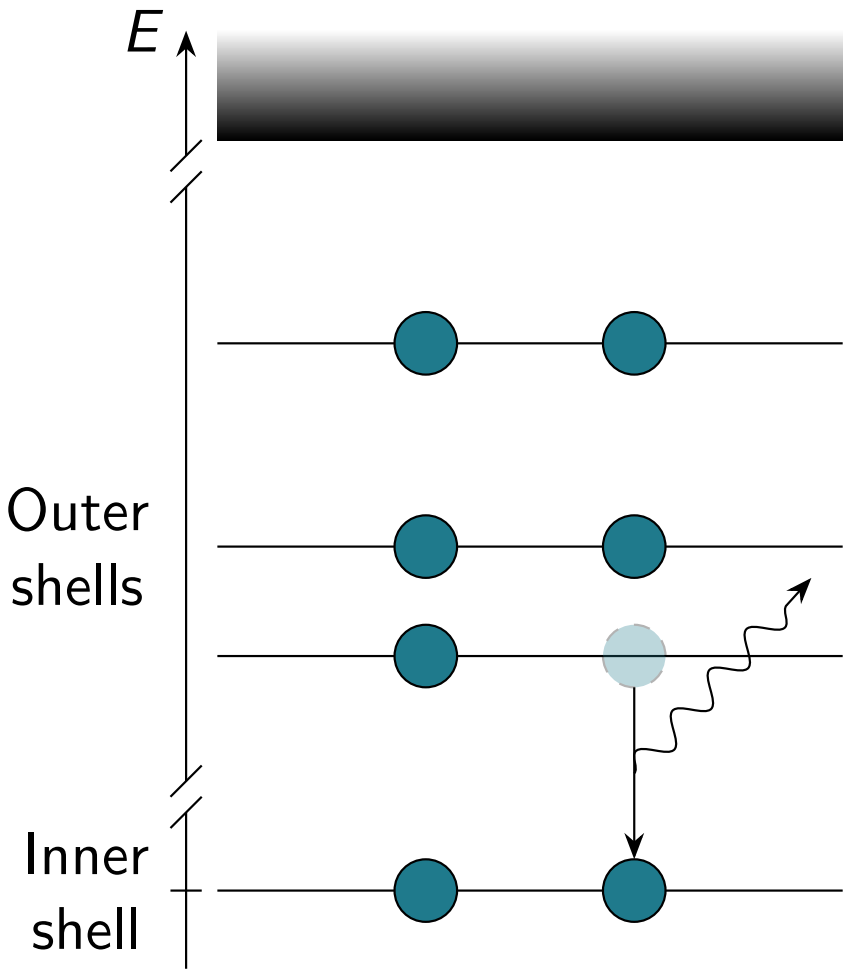

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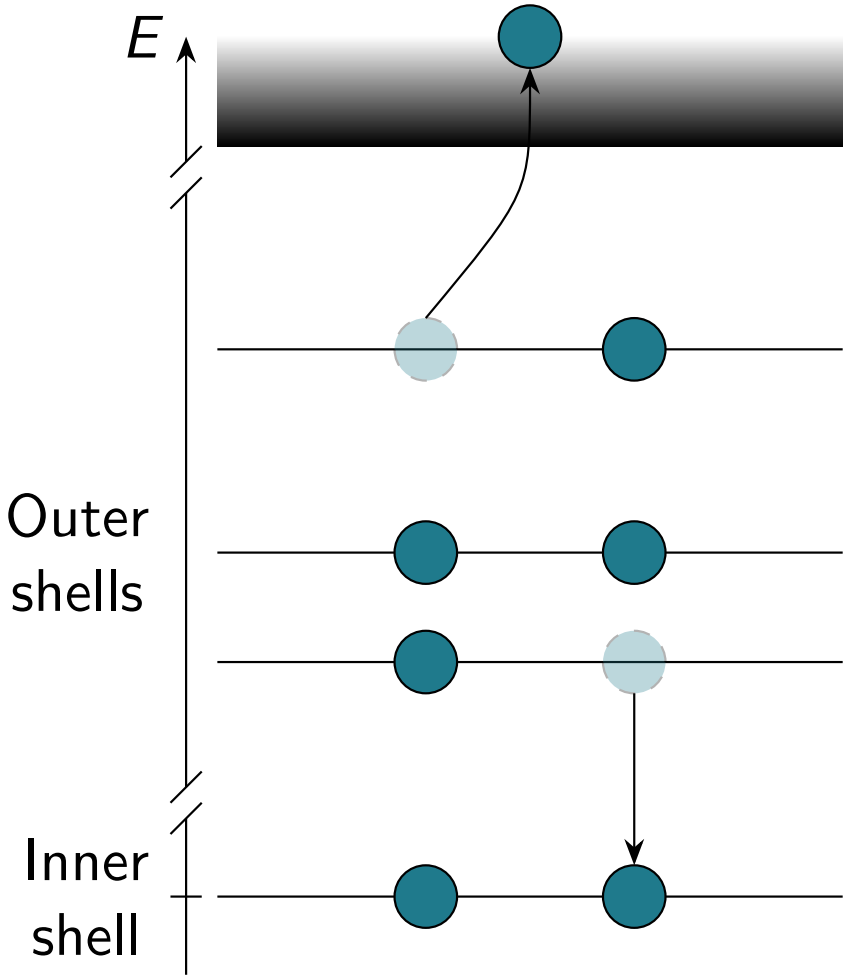

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Alternative processes

Shake processes

Post-ionization, the different number of particles in the system leads to a change in the Hamiltonian. This leads to the lack of orthogonality between non-equivalent states and free-wave wavefunctions in the initial and final configurations.

$$\langle 1s_i | 2s_f \rangle \neq 0 \qquad \left\langle 1s_i \middle| e^-_{free} \right\rangle \neq 0$$

Shake-up

Excitation of extra electron(s).

Shake-off

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Shake Processes

The probability of these processes occurring is extremely dependent on the incident energy.
Since for this thesis, the energy ranges studied were below the ionization threshold, no shake processes were accounted for.

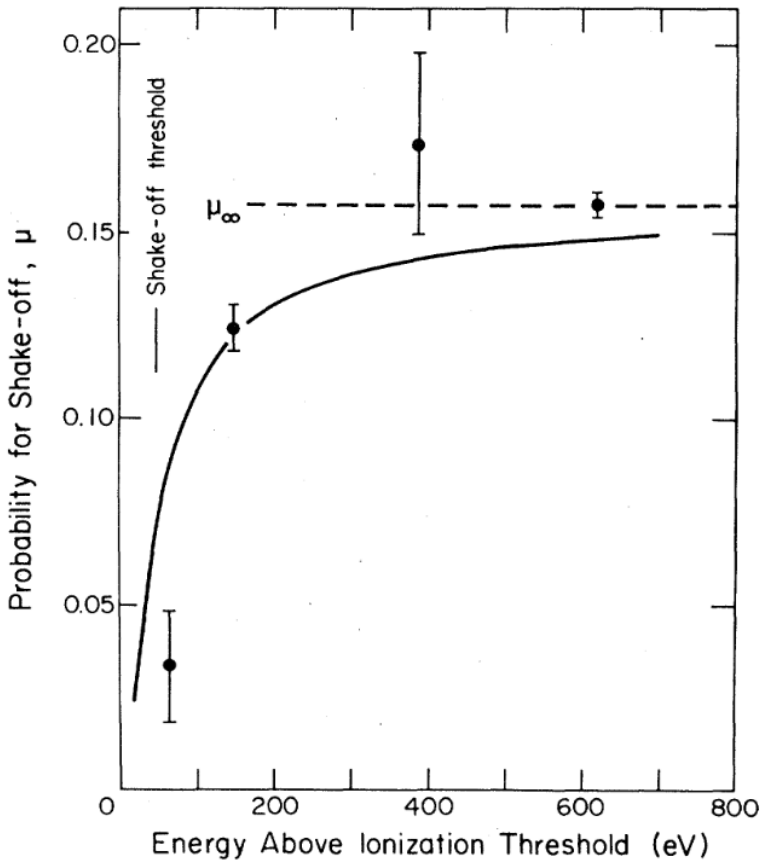
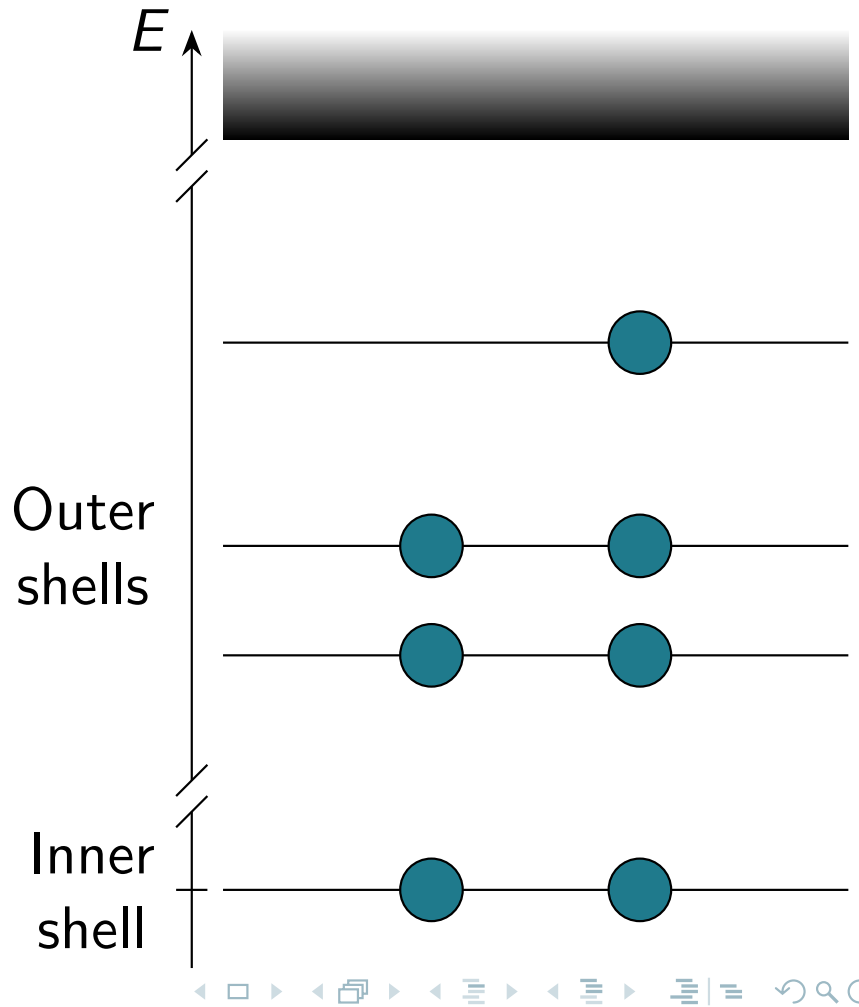


Figure: Thomas model for shake probability. [1]

Other processes

Photoexcitation

The most relevant process, for the scope of this work, is that of resonant photoexcitation. In it, instead of a vacancy generated due to sending one electron to the continuum, it has, in turn, remained bound but in a higher energy level.



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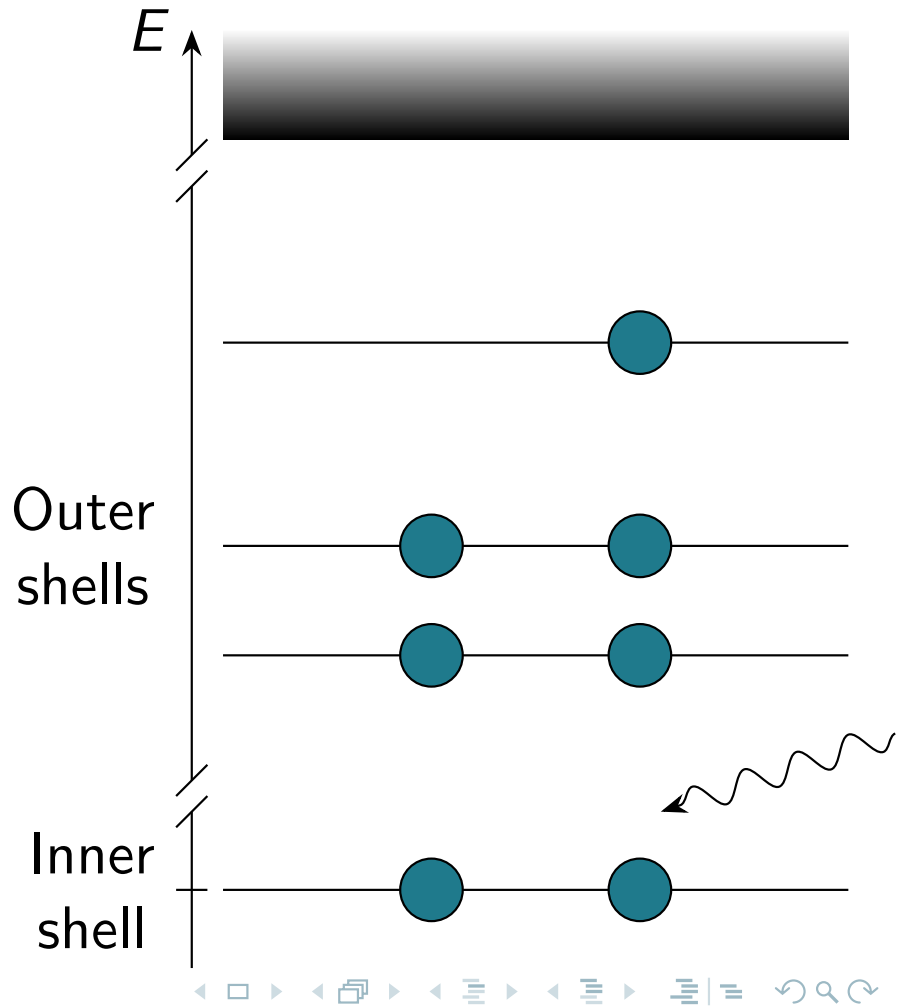

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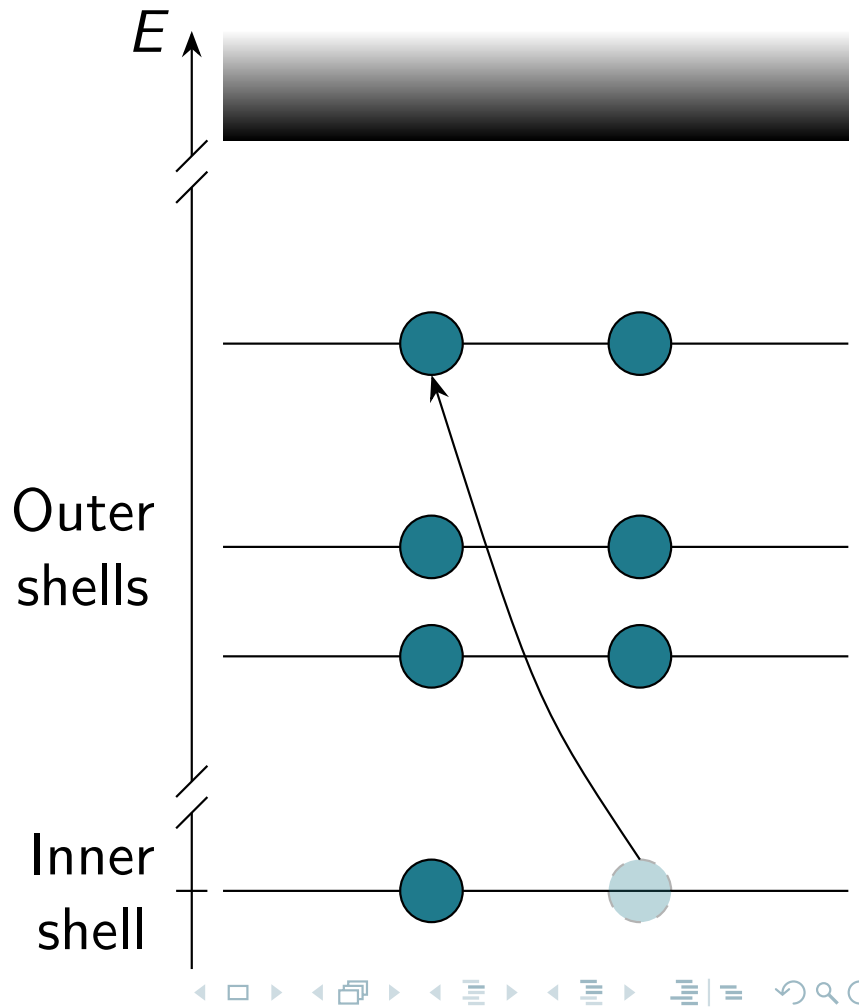

Schrödinger's Hamiltonian

In its most basic form, for a "classical" atom (nucleus + electrons), and when relativistic effects are not taken into account, the considered Hamiltonian follows the one use in Schrödinger's equation:

$$\hat{H} = \sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_{j>i} \frac{1}{r_{ij}}$$

It incorporates:

- The kinetic energy of the electron.
- The potential energy of the electron-nucleus attraction.
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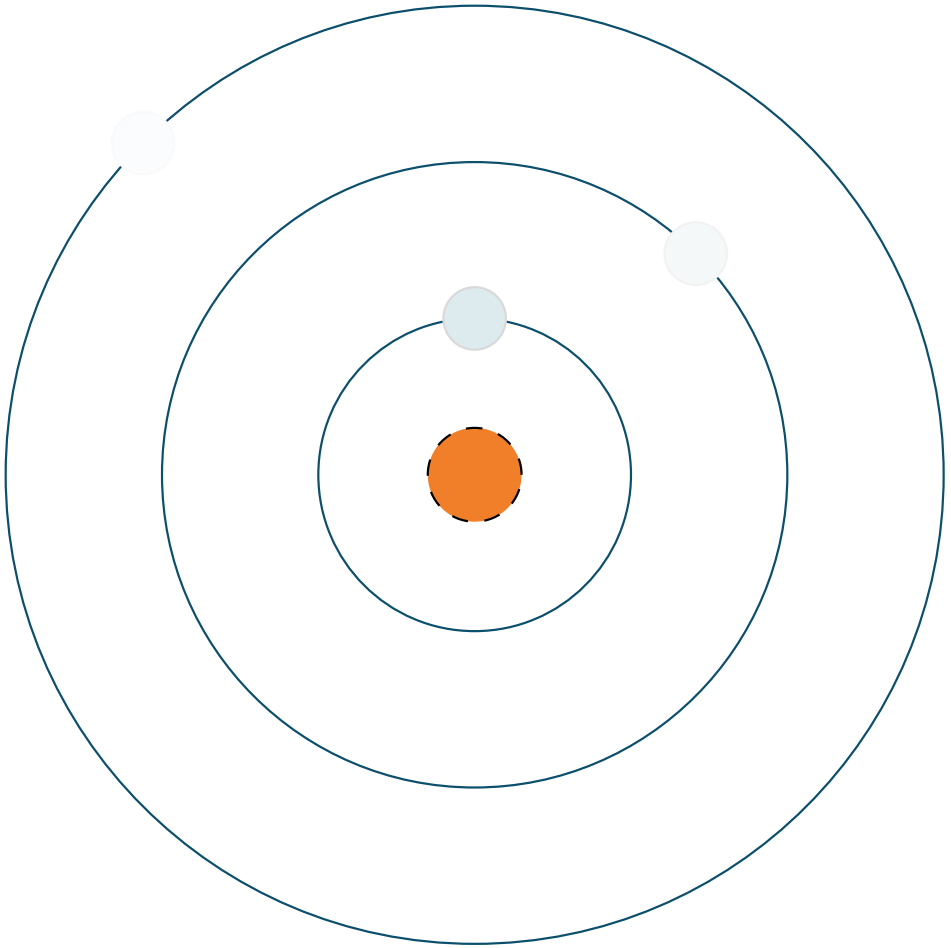
Solving the non-relativistic many-body problem

Due to the complexity introduced by the many bodies in the system, and their interactions, a numerical method needs to be employed as to obtain eigenfunctions for this Hamiltonian.



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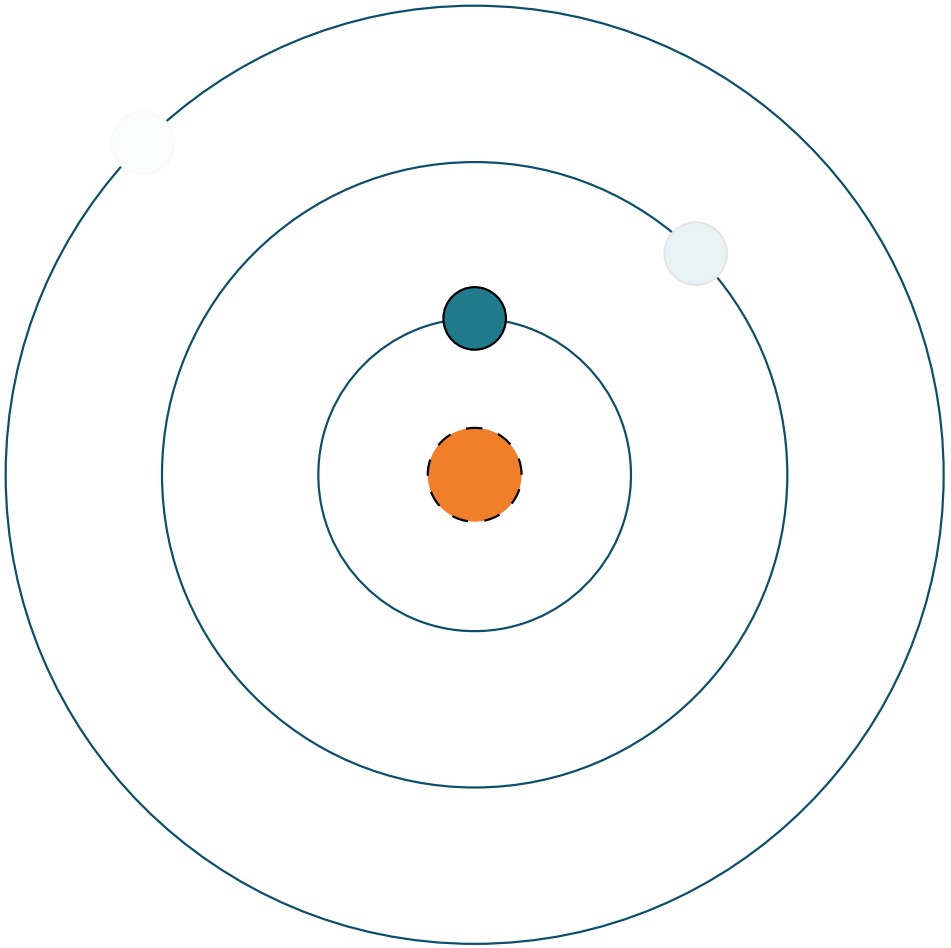

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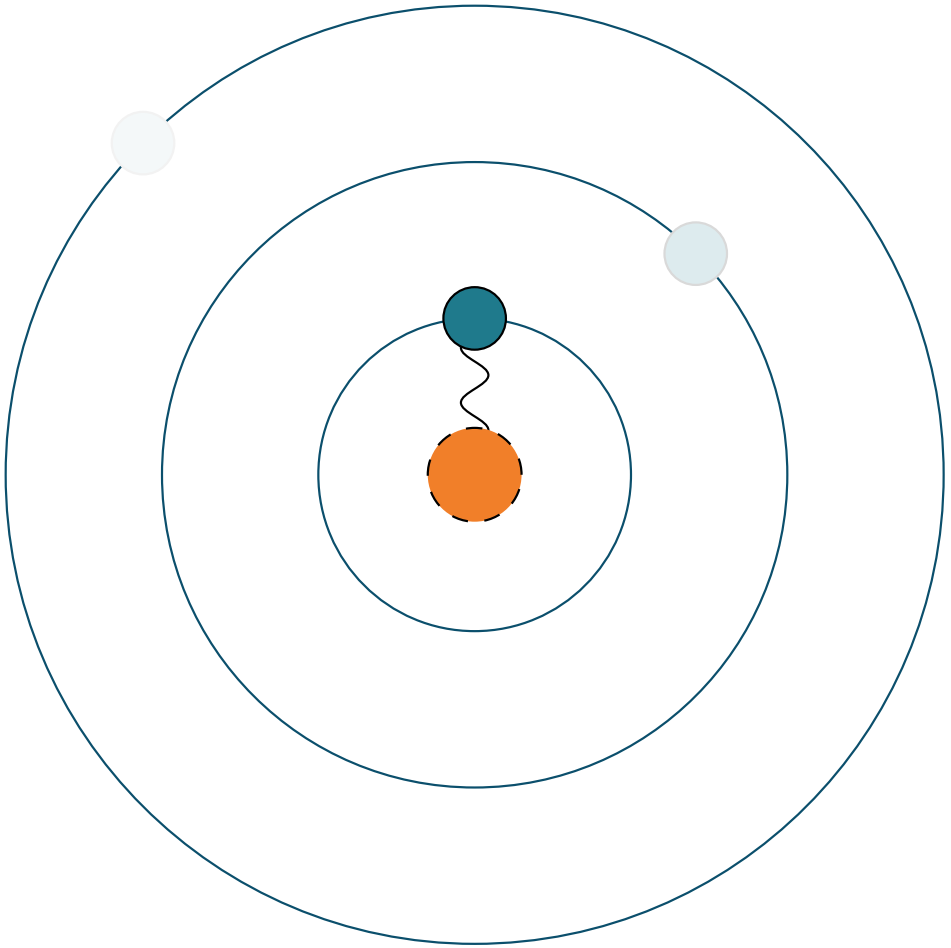

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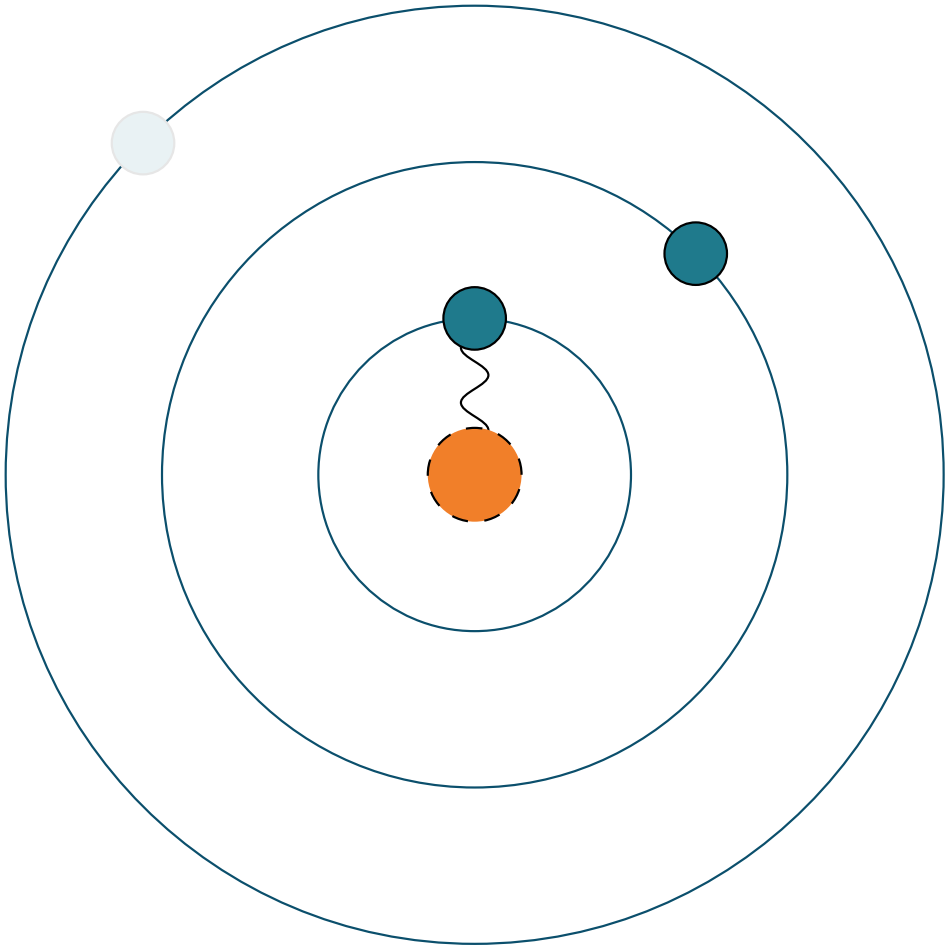

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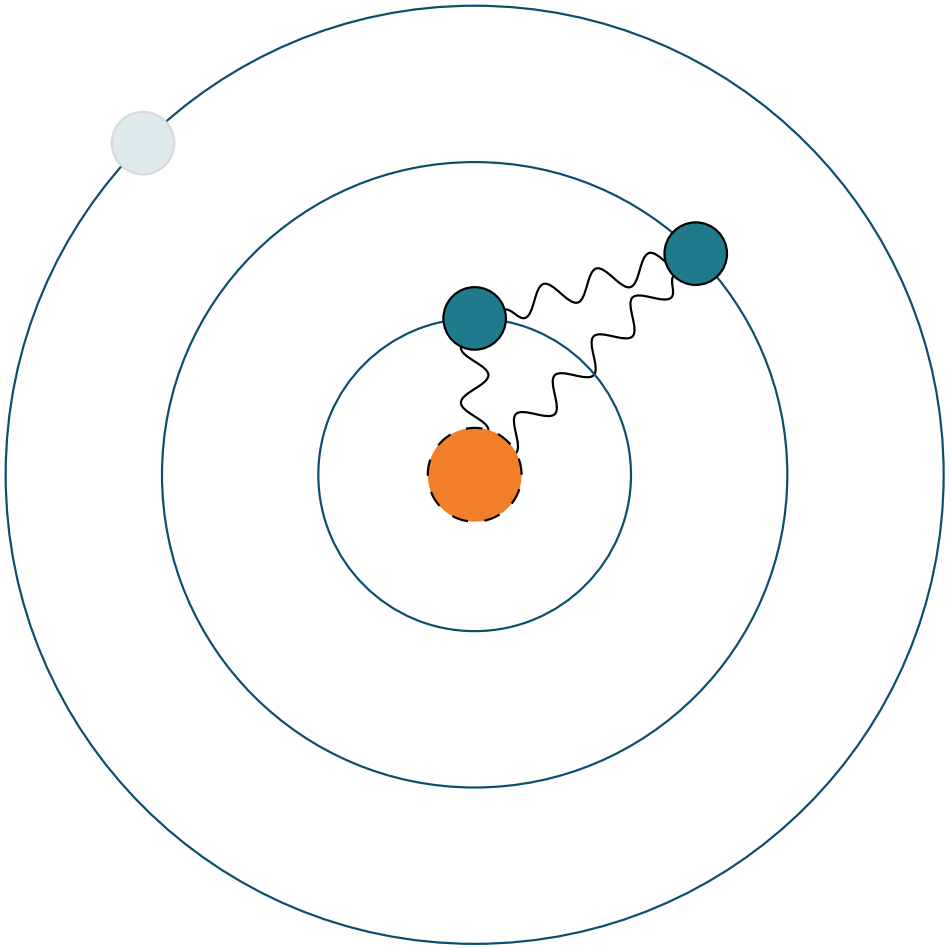

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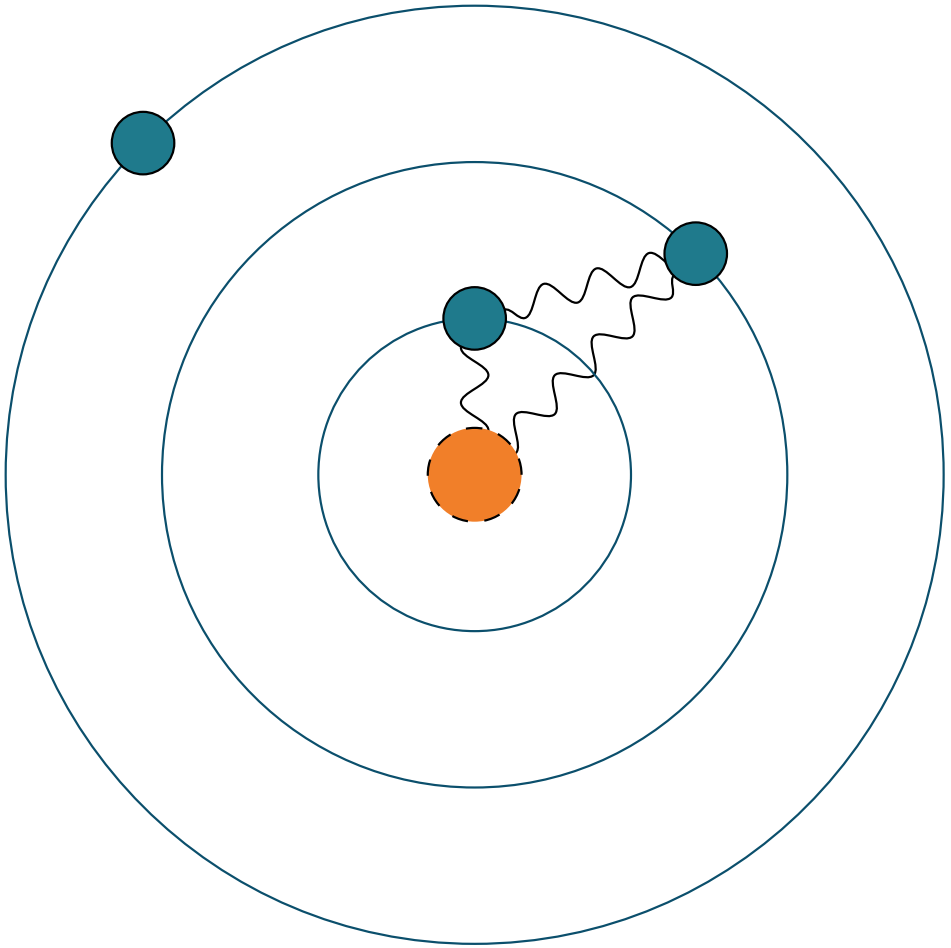

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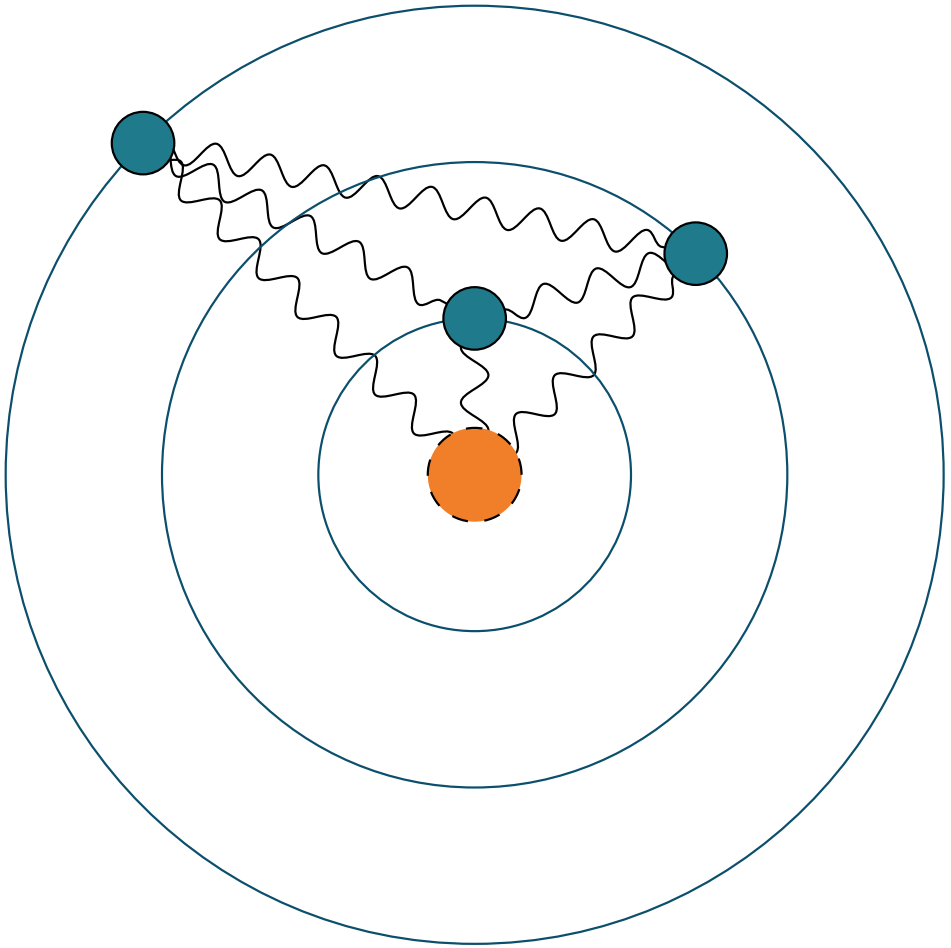


Solving the non-relativistic many-body problem

Each of the electrons' wavefunctions, u, are composed as a product of a spatial part, ψ, and one related to the electron's spin χ.

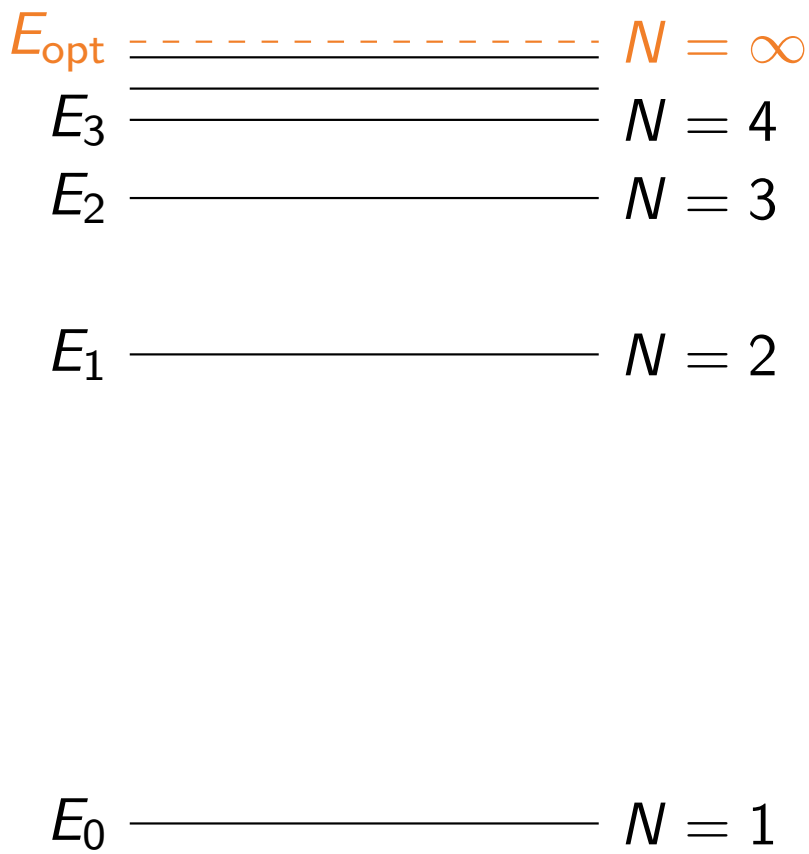
$$u = \psi\chi$$

The system's wavefunction should then be written as a Slater determinant as to account for anti-symetry and the fermionic nature of the electrons.

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} u_1(x_1) & u_2(x_1) & \dots & u_N(x_1) \\ u_1(x_2) & u_2(x_2) & \dots & u_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_1(x_N) & u_2(x_N) & \dots & u_N(x_N) \end{vmatrix}$$

Solving the non-relativistic many-body problem

Through a self-consistent field approach, the method solves, for each cycle, a set of integro-differential equations as a way to compute new wavefunctions and the new energy for the system.



Solving the non-relativistic many-body problem

This process is then repeated up until the energy difference in-between two steps is under a pre-defined benchamark value, as to assure the computation has converged.

METER DIAGRAMA DE BLOCOS

Limitations of the non-relativistic approach

While Schrodinguer's equation may be quite accurate for low energy systems (e.g. Hydrogen), where the speed of the surrounding electrons is not comparable to that of light, such is not the case for more complex and heavier systems.

Speed of 1s electrons in ground state configurations (% of c)

Hydrogen:	0.516%
Copper:	14.883%

Overview

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Conclusion

Thank you
for your attention!