Relativistic coupled-cluster response theory for closed-shell molecules.

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May 24, 2023

Presentation Outline

1. **CV**

2. **PhD project**

3. **Other projects**

4. **Conclusion**

CV

Personal informations

- **Full name**: Gabriele Fabbro
- **Date and place of birth**: 10 November 1998, Pordenone (Italy)
- **Citizenship**: Italian

Education

- **Bachelor's degree in Chemistry** (grade: 110/110), Trieste.
- **Master's degree in Theoretical Chemistry** (grade: 110/110 *cum laude*), Trieste.
- **PhD in Theoretical Chemistry** (ongoing), Toulouse.

CV

Topics

- **Bachelor's thesis project**: NEXAFS spectroscopy to study naphtalen boronic acids using DFT.

    - Supervisor: Prof. Daniele Toffoli (Trieste)

- **Master's thesis project**: analysis and calculation of electric field gradient in molecules in relativistic frameowrk.

    - Supervisor: Prof. Mauro Stener (Trieste)
    - Co-Supervisor: Dr. Trond Saue (Toulouse)

- **PhD thesis project**: relativistic coupled-cluster response theory for closed-shell molecules.

    - Supervisor: Dr. Trond Saue (Toulouse)

PhD project
General overview

- The thesis is part of the project **HAMP-vQED** [Highly Accurate Molecular Properties using variational Quantum Electrodynamics][1].

- Heavy elements need the **special theory of relativity** to be understood.
- HAMP-vQED project will investigate the possible role of **quantum electrodynamics (QED)** in chemistry.

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[1] https://dirac.ups-tlse.fr/hamp-vqed/doku.php?id=public:overview

PhD project
General overview

- Some QED effects:
    - **Vacuum polarization**: A charge in space is surrounded by virtual electron-positron pairs.
    - **Self-energy**: A charge drags along its electromagnetic field.
    - **Lamb shift**: splitting between the $^2S_{1/2}$ and $^2P_{1/2}$ states of one-electron atoms, not predicted by the Dirac equation.
        - $\rightarrow$ Hydrogen: 4 meV
        - $\rightarrow$ Uranium: 468 eV
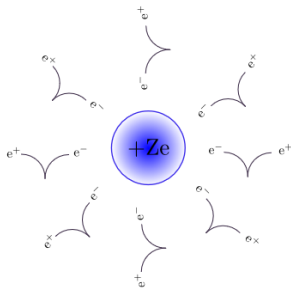
PhD project
General overview

- HAMP-vQED will provide a computational protocol for the **highly accurate computation of molecular properties**.

- To obtain extremely accurate results it is necessary to use an extremely accurate method: **coupled-cluster theory**.
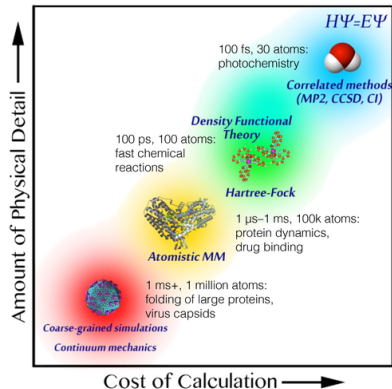
Figure 1: Source: https://education.molssi.org/
mm-tools/01-introduction/index.html

PhD project
Coupled-cluster theory

- In coupled-cluster theory we use a **non-unitary exponential parametrization** to define our CC wave function:

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Phi_0\rangle \ , \ \ \hat{T} = \sum_{\mu} t_{\mu} \hat{\tau}_{\mu} \tag{1}$$

PhD project
Coupled-cluster theory

- In coupled-cluster theory we use a **non-unitary exponential parametrization** to define our CC wave function:

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- Taking the expectation values of the CC wave function we see that the CC energy is a function of the amplitudes:

$$E = \frac{\langle \Psi_{CC} | \hat{H}_N | \Psi_{CC} \rangle}{\langle \Psi_{CC} | \Psi_{CC} \rangle} \equiv E(\{t_{\mu}\}) \tag{2}$$

where $\hat{H}_N$ is the **normal-ordered Hamiltonian**, defined in the following way:

$$\hat{H}_N = \sum_{pq} f_{pq} \{a_p^{\dagger} a_q\} + \frac{1}{2} \sum_{pqrs} \langle pq||rs \rangle \{a_p^{\dagger} a_q^{\dagger} a_s a_r\} \tag{3}$$

PhD project
Coupled-cluster theory

- We can overcome to this problem by projection:

$$\hat{H}_N \ket{\Psi_{CC}} = E_{CC} \ket{\Psi_{CC}}$$

$$\hat{H}_N e^{\hat{T}} \ket{\Phi_0} = E_{CC} e^{\hat{T}} \ket{\Phi_0}$$

$$\underbrace{e^{-\hat{T}} \hat{H}_N e^{\hat{T}}}_{\bar{\hat{H}}} \ket{\Phi_0} = E_{CC} \underbrace{e^{-\hat{T}} e^{\hat{T}}}_{=1} \ket{\Phi_0} \tag{4}$$

$$\bar{\hat{H}} \ket{\Phi_0} = E_{CC} \ket{\Phi_0}$$

where we have introduced the **similarity-transformed Hamiltonian** $\bar{\hat{H}}$.

PhD project
Coupled-cluster theory

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$$
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where we have introduced the **similarity-transformed Hamiltonian** $\bar{\hat{H}}$.

- At the end, projecting onto $\langle\Phi_0|$ and $\langle\Phi_\mu|$ we get an equation for the **energy** and for the **amplitudes**:

$$
\langle\Phi_0|\bar{\hat{H}}|\Phi_0\rangle = E_{CC} \tag{5}
$$

$$
\langle\Phi_\mu|\bar{\hat{H}}|\Phi_0\rangle = 0 \ , \ |\Phi_\mu\rangle = \hat{\tau}_\mu |\Phi_0\rangle \tag{6}
$$

PhD project

My tasks

- The **DIRAC code**[2] features two coupled cluster modules:

  1. **RELCCSD** module: it benefits from an extensive treatment of molecular symmetry. This module allows the calculation of expectation values as well as excitation, ionization and electron attachment energies.
  2. **EXACORR** module: is geared for massively parallel calculations.

- In this PhD thesis is planned to merge the two codes, in order to provide powerful tools for further CC development.

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[2] https://www.diracprogram.org/doku.php

PhD project
My tasks

- We shall calculate molecular properties as energy derivatives, connected to expectation values through the **Hellmann-Feymann theorem**:

$$\frac{dE(\varepsilon_x)}{d\varepsilon_x} = \langle \Psi(\varepsilon_x)| \frac{\partial}{\partial \varepsilon_x} \hat{H}(\varepsilon_x)|\Psi(\varepsilon_x)\rangle \tag{7}$$

PhD project
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- In practice the wave function is optimized through electronic (wave-function) parameters (MOs, cluster amplitudes), and for variational wave functions we have:

$$\frac{dE(\varepsilon_x, \kappa)}{d\varepsilon_x} = \frac{\partial E(\varepsilon_x, \kappa)}{\partial \varepsilon_x} + \underbrace{\frac{\partial E(\varepsilon_x, \kappa)}{\partial \kappa}}_{=0} \frac{d\kappa}{d\varepsilon_x} = \frac{\partial E(\varepsilon_x, \kappa)}{\partial \varepsilon_x} \tag{8}$$

PhD project
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- CC theory **is not variational**: we will use the **Lagrangian formalism**.

$$\mathcal{L}^{CC}(\varepsilon_x, t, \lambda) = E_{CC} + \sum_\mu \lambda_\mu \langle \Phi_\mu | \hat{\bar{H}} | \Phi_0 \rangle \tag{9}$$

PhD project
My tasks

- My work is focused on the calculation of **linear response functions**, which are **second derivatives of the energy**: polarizabilities, magnetizabilities, NMR parameters, ...

- Challenge in **magnetic properties**: they in relativistic response theory involve the solutions (orbitals) of the Dirac equation of **negative-energy**[a] (typically discarded): the formulation of a method to calculate these properties is part of the project.

[a] G. Aucar, H. J. Aa. Jensen, T. Saue and L. Visscher, J. Chem. Phys. 110 (1999) 6208
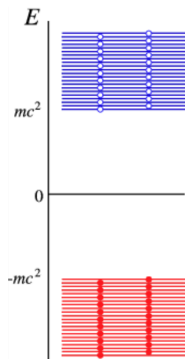
Other projects
Electric field gradient

- Nuclei with spin I>1/2 possess an **nuclear electric quadrupole moment** which measures the deviation from the spherical symmetry of the charge distribution.

- The electric field gradient is **sensitive to deviations from spherical symmetry**, such arising from bond formation:
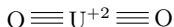
$$e\hat{q} = \frac{3z^2 - r^2}{r^5} = \sqrt{\frac{16\pi}{5}} \frac{Y_{20}}{r^3} \tag{10}$$
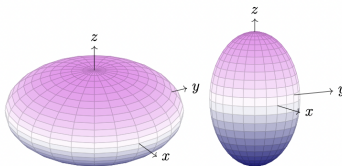
Other projects
Chemical bond in actinyls

- Why UO_2^{2+} is linear and the **isoelectronic** compound ThO_2 is bent?[3]

$$O \equiv U^{+2} \equiv O$$

$$\begin{array}{c} \text{Th} \\ \diagup\!\!\diagup \;\; \diagdown\!\!\diagdown \\ \text{O} \qquad \text{O} \end{array}$$

- For many years, attempts have been made to justify the linearity of the uranyl molecule, and it is still a controversial topic.

- What happens to the geometry of ThO_2 if we **gradually** vary the nuclear charge of Th?

  - ≻ Is there a critical angle where ThO_2 becomes linear?
  - ≻ Does the molecule become linear gradually?

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[3] **Willard R. Wadt J. Am. Chem. Soc. 1981, 103, 20, 6053–6057**

Conclusion

Thank you for your attention
Questions?