



ACCADEMIA NAZIONALE DEI LINCEI

---

CONVEGNO LINCEO

## QUANTUM MECHANICS APPLIED TO EARTH SCIENCES

26-27 MARCH 2025

### ABSTRACT

*Comitato ordinatore:* Vincenzo AQUILANTI (Linceo, Università di Perugia), Luca BINDI (Linceo, Università di Firenze), Giovanni FERRARIS (Linceo, Università di Torino), Massimo INGUSCIO (Linceo, Università Campus Bio-Medico di Roma), Annibale MOTTANA (Linceo, Università degli Studi Roma Tre), Roberta OBERTI (Linceo, Istituto di Geoscienze e Georisorse - CNR Pavia), Giulio Armando OTTONELLO (Linceo, Università di Genova, coordinatore), Antonio SGAMELLOTTI (Linceo, Università di Perugia).

### PROGRAMME

Quantum mechanics applied to Earth Sciences is a fascinating and increasingly important field of study. While traditionally quantum mechanics has been associated more with the realm of particle physics and the study of subatomic particles, its applications to earth sciences have become evident and significant to help us understand the fundamental processes that occur within Earth's geological structures. This includes the behavior of atoms and molecules in minerals, the properties of materials under extreme pressure and temperature conditions, and the mechanisms behind geological phenomena such as earthquakes, volcanic eruptions, and the formation of rocks.

#### Wednesday, 26<sup>th</sup> March

- 14.30 *Welcome addresses from the Presidency of the Academy*
- 15.00 Matteo COCOCCIONI (Università di Pavia): *Hubbard-corrected DFT functionals in the study of thermoelastic properties of minerals*
- 15.40 Donato BELMONTE (Università di Genova): *Thermodynamic and thermophysical properties of minerals in the quasi-harmonic approximation: testing the accuracy of hybrid functionals*
- 16.20 Coffee Break
- 16.35 Bartolomeo CIVALLERI (Università di Torino): *Using localized basis sets to modelling solids: from minerals to porous materials*
- 17.15 Maurizio COSSI (Università del Piemonte Orientale): *Integral equation formalism of the polarized continuum method and its potential applications*

17.55 Carlo GATTI (CNR, Milano): *Electronic localization and delocalization: Implications on terrestrial materials in various states of aggregation*

**Thursday, 27<sup>th</sup> March**

- 9.00 Razvan CARACAS (IPGP, Paris): *Density relations in deep magma oceans*
- 9.40 Giorgio SANGIOVANNI (University of Würzburg): *Iron and Nickel at Earth's core conditions: implications for geomagnetism*
- 10.20 Dario ALFÈ (Università di Napoli Federico II): *The inner core nucleation paradox*
- 11.00 Coffee Break
- 11.15 Piero UGLIENGO (Università di Torino): *Chemical reactivity of interstellar dust*
- 11.55 Artem OGANOV (Skoltech): *Predictive crystallography: new high-pressure compounds and novel phenomena*
- 12.25 Discussion, final remarks and outlooks

ROMA - PALAZZO CORSINI - VIA DELLA LUNGARA, 10  
Segreteria del convegno: [convegni@lincei.it](mailto:convegni@lincei.it) - <http://www.lincei.it>

Tutte le informazioni per partecipare al convegno sono disponibili su:  
<https://www.lincei.it/it/manifestazioni/quantum-mechanics-applied-earth-sciences>

Per partecipare in presenza al convegno è necessaria l'iscrizione online  
Fino alle ore 10 è possibile l'accesso anche da Lungotevere della Farnesina, 10  
I lavori potranno essere seguiti dal pubblico anche in streaming

L'attestato di partecipazione al convegno viene rilasciato esclusivamente a seguito di partecipazione in presenza fisica e deve essere richiesto al personale preposto in anticamera nello stesso giorno di svolgimento del convegno

**Hubbard-corrected DFT functionals in the study  
of thermoelastic properties of minerals**  
Matteo COCOCCIONI (Università di Pavia)

The computational modeling of minerals has established itself as one of the main tools to investigate the physical behavior of the Earth's interior and to connect it to the variation of chemical composition with depth. While the use of ab initio techniques is almost mandatory to capture the large variety of different (and sometimes exotic) phases and properties, the broad ranges of chemical compositions, pressure and temperature conditions still pose significant challenges to these techniques.

In this talk I will discuss the use of density-functional theory (DFT) in this field and, in particular, of Hubbard-based corrections to common approximate exchange-correlation energy functionals, according to the popular scheme named DFT+U. Motivated by the increasing concentration of Fe with depth, the use of these (or similar) corrections is crucial in presence of transition metal ions in order to avoid the consequences of the defective cancellation of electron self-interactions that plagues semilocal functionals (particularly serious for d states) and to make accurate predictions on the stability of various phases, on the transitions between them, and on the thermo-mechanical properties of relevant compositions.

In my presentation I will review some of the most relevant developments that, in the last decades, have been introduced in the formulation of the Hubbard correction. I will discuss, in particular, the definition of an extended formulation (DFT+U+V) including both on-site and inter-site interactions, a linear-response code to evaluate the effective interactions parameters and the consistent evaluation of phonons using density-functional perturbation theory.

While exemplifying these development with their application to selected test cases I will also comment on theoretical aspects and on the comparison with other techniques.

**Thermodynamic and thermophysical properties of minerals in the quasi-harmonic approximation: testing the accuracy of hybrid functionals**  
Donato BELMONTE (Università di Genova)

First principles theory plays a key role in predicting the thermodynamic and thermophysical properties of Earth's materials at high pressure and temperature conditions. Ab initio calculations performed in the framework of quasi-harmonic approximation (QHA) allow for the computation of free energies and thermodynamic functions of mineral phases in a broad range of P-T conditions, thus providing an independent and self-consistent way to check the accuracy of experimental phase boundaries and thermodynamic assessments. In the vast diversity of DFT methods currently implemented in quantum-mechanical codes, hybrid functionals are widely and successfully used nowadays in the field of solid-state chemistry. Nevertheless, these functionals are rarely employed in mineral physics and geophysical studies and their performance at high pressure and temperature conditions is largely unknown. In this work, first principles calculations of the thermodynamic properties of dense magnesium silicates have been carried out with the hybrid B3LYP density functional method in order to get

original insights on phase stability relations in the deep mantle of the Earth. The main mineralogical constituents of the Earth's mantle transition zone (MTZ), namely ringwoodite and majorite garnet, have been considered as relevant case studies since, as a matter of fact, their thermodynamic properties are still poorly defined or affected by large uncertainties. The results provided by B3LYP are then critically compared to modern calorimetric experiments and tested against those obtained by different DFT methods. Potential physical unsoundness of some thermodynamic data currently adopted in the literature is also briefly outlined. The final part of this work highlights how and why phase equilibrium calculations of olivine and garnet phases in the bottom part of the MTZ are able to provide important clues on global-scale mantle convection and on the interpretation of mantle seismic discontinuities.

**Using localized basis sets to modelling solids:  
from minerals to porous materials**

Bartolomeo CIVALLERI (Università di Torino)

In general, the solution of the one-electron Hartree-Fock or Kohn-Sham equations relies on the analytical representation of the one-electron wave functions by a suitable basis set. For solid state calculations, plane waves are usually the most common choice as they are the ideal basis functions for periodic systems [1]. However, localised basis functions, such as atomic orbitals, provide a natural and physically motivated description of the atomic-like features of solids. This offers several advantages related to the locality of the basis functions and the compactness of the basis set [2,3]. Furthermore, they allow efficient calculations with state-of-the-art hybrid HF/DFT functionals and a straightforward analysis of chemical bonding [4].

In this talk, the use of localised atomic orbitals, typically Gaussian-type orbitals, will be highlighted by discussing their implementation in the CRYSTAL code [5], and then selected applications of recently proposed composite HF/DFT hybrid methods [6] to porous materials [7] and to molecular solids relevant as cryominerals in planetary science will be presented.

[1] R.M. Martin. *Electronic Structure: Basic Theory and Practical Methods*. Cambridge University Press; 2004.

[2] C. Pisani ed. *Quantum-Mechanical Ab-initio Calculation of the Properties of Crystalline Materials*, Lecture Notes in Chemistry, Springer-Verlag Berlin, Heidelberg; 1996.

[3] R. Dovesi, B. Civalleri, R. Orlando, C. Roetti, V.R. Saunders. *Ab initio quantum simulations in solid state chemistry*, Rev. Comput. Chem. 21 (2005) 1-125

[4] R. Dovesi, F. Pascale, B. Civalleri, et al. J. Chem. Phys. 152 (2020) 204111

[5] A. Erba, J. Desmarais, S. Casassa, B. Civalleri, et al. J. Chem. Theory Comput. 19 (2023) 6891-6932

[6] L. Donà, J.G. Brandenburg, B. Civalleri, J. Chem. Phys. 151 (2019) 121101; L. Donà, J.G. Brandenburg, I.J. Bush, B. Civalleri. Faraday Discussions 224 (2020) 292-308

[7] L. Donà, J. G. Brandenburg, B. Civalleri. J. Chem. Phys. 156 (2022) 094706

**Electronic localization and delocalization:  
Implications on terrestrial materials in various states of aggregation**

Carlo GATTI (CNR-SCITEC, Milano - Istituto Lombardo,  
Accademia di Scienze e Lettere, Milano)

A detailed understanding of the structure of a material—whether through experimental methods or *in silico* approaches—is crucial for both its study (from a geochemist's perspective) and the discovery of advanced materials or novel materials with unique properties (from a materials scientist's perspective). The geometrical, electronic, and (magnetic) structure of a material is ultimately determined by its chemical bonding, which depends on its chemical composition/stoichiometry and external factors such as applied pressure, temperature, and the presence of external fields. The nature of chemical bonding in a material is closely tied to the localization and delocalization of electrons. Each type of chemical bond (ionic, covalent, metallic, etc.) corresponds to specific patterns of electron localization and delocalization between the bonded centers (e.g., two-center (2c), three-center (3c), or multicenter bonds).

In this talk, I will explore how information about electron localization and delocalization—and thus chemical bonding—can be extracted from a system's wavefunction. As the number of electrons ( $N$ ) increases, the information contained in the wavefunction ( $\Psi$ ) quickly becomes too vast for human comprehension, necessitating the use of information compression techniques. Two main approaches are typically employed for this purpose [Martín Pendás and Gatti, 2021]. The first approach involves models designed to solve Schrödinger's equation to rationalize  $\Psi$ . One-electron orbital-based descriptions are often used, as managing and manipulating  $N$  three-dimensional functions is far more practical than dealing with  $\Psi$  directly. However, this simplification has certain limitations. Orbitals are not unique due to the infinite number of transformations that leave the total  $\Psi$  invariant, and they are also highly method-dependent. The second approach compresses the information in  $\Psi$  by leveraging its probabilistic interpretation. This method leads to the extraction of real-space functions, such as electron density (ED), the Laplacian of the electron density, electrostatic potential, and the Electron Localization Function (ELF) [Becke and Edgecombe, 1990; Savin *et al.*, 1997]. By analyzing these scalar functions in terms of their gradients using the theory of gradient dynamical systems [Abraham and Shaw, 1992] well-defined space partitionings emerge, allowing for a natural study of these scalar fields in terms of their topology. This leads to Quantum Chemical Topological (QCT) approaches, providing a wealth of physically unbiased descriptors, such as the Source Function (SF) [Bader and Gatti, 1998; Gatti, 2024] in terms of ED, or Localization and Delocalization Indices based on pair electron density [Fradera *et al.*, 1999]. These indices express the number of electrons fully localized in a given basin and those shared or exchanged between two or more basins [Gatti, 2005; Gatti and Macchi, 2012a; Saleh *et al.*, 2019].

Following a general introduction, some of the descriptors mentioned above will be discussed in detail, along with their applications to terrestrial materials. Applications of ELF and ED to the study of proton docking sites in silica polymorphs [Gibbs *et al.*, 2003], electron delocalization leading to the formation of the F-center (color center) in sodium electro sodalite [Madsen *et al.*, 1999], and a direct space representation of electron delocalization in metals [Silvi and Gatti,

2000] will be presented. Localization and delocalization indices will be applied to study the effects on energetics, electron delocalization, and bonding in aluminosilicates when charge-compensating cations are introduced into their framework (Gatti *et al.*, 2012b). These indices will also be used to detect multicenter bonding or, through ELF, charge-shift bonds in simple terrestrial materials [Shaik *et al.*, 2005].

Examples of the Source Function's applications will include evaluating the debate on ionicity vs. hypervalency in crystalline K-sulphate [Schmøkel *et al.*, 2012], characterizing localized vs. delocalized bonding in  $\gamma$ -Boron (the ionic high-pressure form of Boron) (Oganov *et al.*, 2009; Saleh *et al.*, 2019), and detecting electron conjugation effects in molecular and crystalline benzene.

In recent years, advancements in technical methods have made the application of localization and delocalization indices feasible in condensed phases [Golub and Baranov, 2016; Otero-de-la-Roza *et al.*, 2018]. Their use in revealing the connection between electron localization/delocalization in chalcogenide phase-change materials and their contrasting properties in the amorphous and crystalline phases will be briefly discussed [Raty *et al.*, 2019; Raty *et al.*, 2024]. If time permits, I will also highlight recent developments in disclosing electron localization/delocalization patterns, such as the introduction of the electron distribution function [Martín Pendás and Francisco, 2019], real-space analogs of Pauling resonance structures in molecules and crystals, and the detection [Menéndez-Herrero *et al.*, 2025] of Born probability maxima to identify the most likely positions of the  $N$  electrons in a system. These topics will be illustrated with simple examples.

## References

- Abraham, R. H. and Shaw, C. D. (1992) *Dynamics: The Geometry of Behavior*, Addison Wesley: Redwood City, CA
- Bader, R. F. W.; Gatti, C. (1998) A Green's function for the density. *Chem. Phys. Lett.* 287, 233–238.
- Becke A. and Edgecombe K. E. (1990) A simple measure of electron localization in atomic and molecular systems. *J. Chem. Phys.* 92, 5397-5403
- Fradera, X.; Austen, M. A.; Bader, R. F. W. (1999) The Lewis Model and Beyond. *J. Phys. Chem A* 103, 304–314.
- Gatti, C. (2005) Chemical bonding in crystals: new directions. *Z. Kristallogr.* 220, 399–457
- Gatti, C. (2024) The Source Function Concept in Chemistry, vol. 2, pages 95-121, in *Comprehensive Computational Chemistry*, Eds R.J. Boyd and M. Yanez, Elsevier
- Gatti, C. and Macchi, P. (2012a) A guided tour through modern charge density analysis, chapter 1, pages 1-78, in *Modern Charge Density Analysis*, C. Gatti and P. Macchi (Eds), Springer, Dordrecht Heidelberg London New York
- Gatti, C.; Ottonello, G.; Richet, P. R. (2012b) Energetics and Bonding in Aluminosilicate Rings with Alkali Metal and Alkaline-Earth Metal Charge-Compensating Cations, *J. Phys. Chem. A*, 116, 8584-8598
- Gibbs, G. V.; Cox, D. F.; Boisen Jr, M. B.; Downs, R. T.; Ross, N. L. (2003) The electron localization function: a tool for locating favourable docking sites in the silica polymorphs. *Phys. Chem. Minerals* 30, 305-316
- Golub, P. and Baranov, A. I. (2016) Domain overlap matrices from plane-wave-based methods of electronic structure calculation. *J. Chem Phys.* 145, 154107

- Madsen, G. K. H.; Gatti, C.; Iversen, B. B.; Damjanovic, L.; Stucky, G. D.; Srdanov, V. I. (1999) F center in sodium electrosodalite as a physical manifestation of a non-nuclear attractor in the electron density. *Phys. Rev. B* **59** 12359–12369
- Martín Pendás Á. and Francisco, E. (2019) Chemical Bonding from the Statistics of the Electron Distribution. *ChemPhysChem* **20**, 2722
- Martín Pendás Á. and Gatti C., (2021). Quantum Theory of Atoms in Molecules and the AIMAll software. In: *Complementary Bonding Analysis* (S. Grabowsky, ed.), De Gruyter, Berlin, Boston, 43-74
- Menéndez-Herrero, M.; Francisco, E. and Martín Pendás, A. (2025) Linnett is Back: Chemical Bonding through the Lens of Born Maxima, *Journal of Chemical Theory and Computation* **21**, 2448-2461
- Oganov, A.; Chen, J.; Gatti, C. *et al.* (2009) Ionic high-pressure form of elemental boron. *Nature* **457**, 863–867
- Otero-de-la-Roza, A.; Pendás, A. M. and Johnson, E.R. (2018) Quantitative electron delocalization in solids from maximally localized Wannier functions. *J. Chem. Theory Comput.* **14**, 4699-4710
- Raty, J.-Y.; Schumacher M.; Golub P.; Deringer V. L.; Gatti C and Wuttig M. (2019). A Quantum-Mechanical Map for Bonding and Properties in Solids. *Adv. Mater.* **31**, 1806280 (6 pages)
- Raty, J.-Y.; Bichara, C; Schön, C. F.; Gatti C and Wuttig M. (2024) Tailoring chemical bonds to design unconventional glasses *Proc. Natl. Acad. Sci. U.S.A.* **121** e2316498121
- Saleh G., Ceresoli D., Macetti G., Gatti C (2019). Chemical Bonding Investigations for Materials. In: *Computational Materials Discovery* (A.R. Oganov, G. Saleh, A.G. Kvashnin, ed.), The Royal Society of Chemistry, London, 117-175
- Savin, A.; Jepsen, O.; Flad, J.; Andersen, O. K.; Preuss, H.; von Schnering, H. G. (1992) Electron Localization in Solid-State Structures of the Elements: the Diamond Structure. *Angew. Chem. Int. Ed. Engl.* **31** (1992) 187–188.
- Shaik, S.; Danovich, D.; Silvi, B.; Lauvergnat, D.L. and Hiberty, P.C. (2005) Charge-Shift Bonding—A Class of Electron-Pair Bonds That Emerges from Valence Bond Theory and Is Supported by the Electron Localization Function Approach. *Chemistry – A European Journal*, **11**, 6358-6371
- Schmøkel, M.S.; Cenedese, S.; Overgaard, J.; Jørgensen, M.R.V.; Chen, Y-S; Gatti, C.; Stalke, D. and Iversen, B.B. (2012) Testing the Concept of Hypervalency: Charge Density Analysis of K<sub>2</sub>SO<sub>4</sub>, *Inorg. Chem.* **51**, 8607-8616
- Silvi, B.; Gatti, C. (2000) Direct Space Representation of the Metallic Bond. *J. Phys. Chem.* **A104** 947–953

## **Iron and Nickel at Earth's core conditions: implications for geomagnetism**

Giorgio SANGIOVANNI (University of Würzburg)

In this talk I am going to start from the electronic properties of Iron and Nickel as two prototypical quantum magnets and I am then going to analyse the influence of external pressure ranging from ambient conditions to the values reached at the Earth's core. I will use realistic many-body calculations to illustrate how flat-band regions in the momentum-energy dispersion of Nickel play a crucial role for its many-body nature. The final part will be dedicated to the potential impact on the mechanism at the basis of the geodynamo.

### **The inner core nucleation paradox**

Dario ALFÈ (Università di Napoli Federico II)

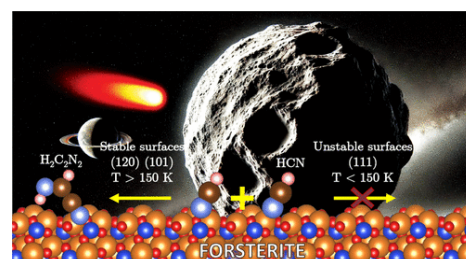
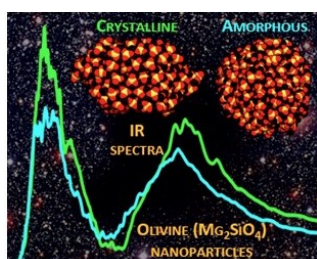
The Earth's solid inner core plays a fundamental role in determining the past and present properties and dynamics of the Earth's deep interior. Inner core growth powers the geodynamo, producing the protective global magnetic field, and provides a record of core evolution spanning geological timescales. However, the origins of the inner core remain enigmatic. Traditional core evolution models assume that the inner core formed when the core first cooled to its the melting temperature, but this neglects the physical requirement that liquids must be supercooled to below their melting point before freezing. Prior estimates from mineral physics calculations of the supercooling  $\delta T$  required to homogeneously nucleate the inner core from candidate binary alloys exceed constraints of  $\delta T \lesssim 400$  K inferred from geophysical observations, while a plausible scenario for heterogeneous nucleation has yet to be identified. Here we consider a different possibility, that atomic-scale compositional fluctuations can increase the local melting temperature, and hence supercooling, available for homogeneous nucleation. Using molecular dynamic simulations of Fe-O alloys we find that compositional fluctuations producing O-depleted regions are too rare to aid nucleation, while O-enriched regions can reduce the undercooling by  $\sim 50$  K ( $\delta T \sim 700$  K) for a bulk concentration of 20 mol%O or  $\sim 400$  K ( $\delta T \sim 300$  K) for a bulk concentration of 30 mol% O. While these results do not explain the nucleation of Earth's inner core, they do show that compositional fluctuations can aid the process of homogeneous nucleation.

### **Chemical reactivity of interstellar dust**

Piero UGLIENGO (Università di Torino)

Interstellar space is not empty, but filled with atoms in different regions (HII, WIM, HIM) and types of "clouds" with different temperatures and densities. The most interesting are the molecular dense clouds, which span tens of parsecs in size and consist mainly of molecular hydrogen ( $H_2$ ), with CO and other trace molecules,  $T=10-20$ K and densities of  $\sim 10^2$  to  $10^6$  molecules/cm<sup>3</sup>. Remarkably, dust grains are also present in about 1% of the total molecular content of the molecular cloud, ranging from 5 nm to 0.25  $\mu$ m in size, resulting from the chemical aggregation of either the carbon atoms (amorphous carbon grains) ejected from the red giant stars, or the silicon, iron, oxygen and magnesium atoms (amorphous olivine-like grains) from the supernova-II explosions. Important chemical synthesis takes place at the grain surface, producing more than 320 different types of molecules (including water) that have been detected spectroscopically in the gas phase after desorption from the grains. The molecular cloud undergoes contraction due to its own gravity, and the collisions between the grains enriched with molecules initially form pebbles, which evolve into planetesimals up to large planets, while at the centre of the cloud a new star is born, as in our planetary system. Understanding the chemical evolution and role of interstellar dust cores is therefore crucial to elucidate the way in which olivine-like bulk material present in asteroids and comets may play a catalytic role in the formation of building blocks relevant to prebiotic chemistry, including water. Indeed, analysis of samples returned from comet 67P and asteroid Bennu revealed a mineral composition rich in olivine and

pyroxene, together with other mineral components such as sulphides and phyllosilicates, and many chemical species relevant to the origin of life. Ab initio computer simulations, with their generality and accuracy, can help to elucidate the spectroscopic and structural features of interstellar grains, and provide clues to the chemical reactivity of olivine minerals for catalysing the formation of nucleobases from HCN, an abundant molecule in the interstellar and cometary context. In this paper, I will present a summary of recent results<sup>1-4</sup> devoted to the molecular simulation of both the structure and spectroscopic features of interstellar core-grains and the reactions of HCN catalysed by the surfaces of crystalline forsterite as a model of the mineral phase of comets and asteroids.



**Figure 1:** **Left:** IR spectra of models of grain core. **Right:** crystalline forsterite reacting with HCN

#### References:

- [1] L. Zamirri et al. *ACS Earth Space Chem.* 2019, 3, 2323–2338.
- [2] N. Bancone, et al. *Phys. Chem. Chem. Phys.* 2023, 25, 26797–26812.
- [3] N. Bancone, et al. *ACS Earth Space Chem.* 2025, 9, 303–313.
- [4] N. Bancone, et al., *J. Phys. Chem. C.* 2024 128, 15171–15178.