

# TOWARDS ROUTINE ORBITAL-FREE LARGE-SCALE QUANTUM-MECHANICAL MODELING OF MATERIALS

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## 1 Overview of the Field

The workshop aimed to bring together researchers who work in fields related to orbital-free density functional theory, OF-DFT. OF-dFT is an ab initio simulation method that holds the promise of revolutionizing, within a couple decades if not earlier, the way atomistic modeling is done and perceived in many practically important applications.

The current status of atomistic (i.e. explicitly considering properties and dynamics of constituent atoms in a material or molecule) materials modeling is that small-scale simulations up to about  $10^3$  atoms are done with Kohn-Sham (KS) DFT (Kohn 1965) with which structures, electronic structures, light absorption properties etc. can be computed. KS DFT relies on the familiar concept of electron orbitals, which on one hand facilitates achieving mechanistic insight but on the other hand makes the calculation expensive. It is the need to compute orbitals (solving the Kohn-Sham equation by building and diagonalizing the Kohn-Sham Hamiltonian) that leads to near-cubic scaling of the CPU cost with system size, with large prefactors to boot. Because KS DFT is formally near-cubically scaling with system size, "large-scale" (as far as atomistic simulations are concerned) simulations from many thousand into millions of atoms and more are done with molecular dynamics (MD) that

- can model structures but not electronic structure or excitation (optical properties) or mechanisms of reactions of ion-host interactions etc,

- relies on interatomic potentials or force fields (FF) that are simplistic representations of the electronic energy as a function of atomic positions. The force fields need calibration by experimental or ab initio data. In particular, *direct* validation of the shape of the FF function has to use an ab initio reference, which practically means DFT except for small molecules.

As many phenomena (i) are intrinsically large-scale (microstructure-driven phenomena such as mechanical properties of alloys, disordered systems, large molecules, polymers, interfaces, etc.), (ii) require ab initio insight (for example the distribution of charges during redox reactions or nature of optical excitations), this presents a significant problem in computational materials modeling that large-scale ab initio methods strive to address. While approaching to improve the scaling of Kohn-Sham DFT are also pursued (Ratcliff 2020, Haynes 2006, Soler 2002, Nakata 2020), they still require substantial CPU cost. It is OF-DFT (Mi 2023, Xu

2024) that is particularly promising for large-scale materials modeling as it can achieve not only near-linear scaling with system size but also small prefactors, enabling *routine* large-scale ab initio calculations with models with hundreds of thousands of atoms doable on a desktop workstation and millions atoms and beyond doable on supercomputers. The key proposition of OF-DFT is the computation of the total energy of a system of ionic cores and electrons from the electron density alone without recourse to orbitals. While the key difference with KS DFT and key challenge is the expression of the kinetic energy component of the total energy – the only energy component that must be expressed via orbitals in KS DFT – as a functional of electron density alone, a number of afferent challenges arise, not the least that of replacing the entire ecosystem of orbital-based analyses with that based on electron densities (Koch 2021, 2024).

If the theoretical capabilities of OF-DFT were unleashed in applied calculations of sufficient accuracy, the entire field of computational materials science would be revolutionized. For example, not only *description* of phenomena, but direct in silico *design* of materials, including materials with key properties relying on intrinsically large-scale phenomena (e.g. alloys, from the ubiquitous steels to non-ferrous alloys), would become infinitely easier.

Unfortunately, OF-DFT is not yet accurate enough to replace KS DFT in many applications. Key issues include the accuracy of kinetic energy functionals (KEF), the availability and accuracy of local pseudopotentials (LPP) (functions that replace Coulombic potentials of atom cores to make calculations easier), and difficulties of computing electronic excitations and of analysis of calculation results (e.g. of reaction mechanisms) in the absence of orbitals. Resolving these difficulties requires a joint effort of theoretical chemists, physicists, as well as mathematicians and computer scientists, and many of the problems are of fundamental nature, and some of the problems could be addressed with data-driven approaches such as machine learning. This workshop brought together experts from different subfields that feed into the development of OF DFT, which is an intrinsically multidisciplinary area, as well as experts in applied modeling that can benefit from OF-DFT.

There is also an economic and societal aspect to improving the OF-DFT method to the extent that it becomes applications-ready, and to developing associated end-user software: the use of KS DFT for large systems despite its unfavorable scaling triggers enormous CPU and other costs in all countries having a research ecosystem of any advanced level (i.e. having large supercomputers available to researchers). Making OF-DFT accurate enough so that many types of calculations could switch to it would greatly reduce that cost on top of all other benefits the method can bring. Availability of OF-DFT solutions accurate enough for use in many applications would also allow the benefits of ab initio modeling to be better used by laboratories and countries, such as developing and regressing countries, that do not provide good supercomputer access to their researchers.

## 2 Recent Developments and Open Problems

The issues mentioned above – accuracy of kinetic energy functionals, the availability and accuracy of local pseudopotentials, and difficulties of computing electronic excitations and of analysis of calculation results and of getting mechanistic insight in the absence of orbitals – constitute open problems that still prevent wide deployment of OF-DFT in most applications, including the applications at moderate scale where current KS DFT is applied at great cost as well as applications which are beyond the realm of feasibility for KS DFT (million atoms and beyond, as in the case of microstructure of alloys or ceramics where models with billions of atoms are desired). In recent years, there have been notable progress in several areas, such as when combined, these have the potential to significantly advance the state of OF-DFT, in particular making it usable in mainstream applied computational materials modeling. These include:

1. Developments in theoretical frameworks of OF-DFT for both KEF and LPP. Developments in alternative formulations of OF-DFT such as DPFT (density potential functional theory) as well as hybrid approaches (for example an OF-DFT – DFTB hybrid presented at the workshop).
2. Developments in OF-DFT software that are already today allowing practitioners to partake of OF-DFT capabilities.

3. Developments in applications of data-driven methods and machine learning to the construction of both the KEF and LPPs.
4. Recent developments in electron density based topology analysis techniques and in density-based analysis of phenomena, as well as developments of electron density based models that are effectively hybrid approaches between OF-DFT and force fields.
5. Developments in other large-scale electronic structure methods that overlap in certain concepts with OF-DFT and offer on one hand algorithmic and numeric approaches that can be adapted for OF-DFT, and on the other hand allow better understanding of respective areas of most promising applicability in applications of alternative large-scale DFT based methods. These techniques also offer opportunities for mutual cross-check and benchmarking which is another outstanding problem in large-scale ab initio calculations.

Researchers from all the above tracks joined the workshop. Many learnt about each other's work for the first time, as many of the above approaches have been developing in parallel in respective communities (which sometimes is true even for different OF-DFT current, as an example below of OF-DFT developments for the nucleus shows, where more cross-fertilization of ideas is desired). All of them feed into the development of OF-DFT and one advantage of this workshop was to bring all these tracks together.

6. Another, practical, issue is the lack of awareness of OF-DFT and its current and advening capabilities among computational materials scientists working on applications. That is why we also brought in researchers working on applied problems, including those who, while not being OF-DFT users or developers, can teach those of the needs that applications face and well as familiarize themselves with what OF-DFT has to offer,

### 3 Presentation Highlights

We present presentation highlights grouped by the pp. 1-6 summarized in the previous section:

1. Developments in theoretical frameworks of OF-DFT for both KEF and LPP. Developments in alternative formulations of OF-DFT such as DPFT (density potential functional theory).

The conference opening and keynote talk was given by Prof. Samuel Trickey from the University of Florida, who has a multidecade experience with OF-DFT as well as KS DFT development and who focused in this talk on how developments in OF-DFT have repercussions on the exchange-correlation functional development on which much of the KS DFT field focused over decades. In particular, with the rise in OF-DFT, there is needs for "de-orbitalization" of exchange-correlation functionals such as meta-GGA functional that can be reformulated as kinetic energy density functionals.

Prof. Weitao Yang from Duke University spoke about the use of orbital free DFT to develop approximations to the exchange-correlation energy functional for conventional Kohn-Sham DFT calculations, such as the development of the localized orbital scaling correction (LOSC) (Li 2018, Mei 2022, Williams 2024) for overcoming systematic delocalization errors in commonly used density functional approximations. He also spoke about modeling of excited states and argued that the electron density alone is insufficient to characterize excited states and that this is a fundamental drawback for orbital-free DFT.

However, Prof. Pavanello of Rutgers university summarized recent developments in computing excited states with OF-DFT with real time dependent methods and with Casida-like time-dependent OF-DFT that he invented. Lack of methods to treat excited states has long been considered as one major drawback of OF-DFT, and that has now changed (Jiang 2021, 2022).

Prof. Wibowo-Teale of University of Nottingham presented a way to obtain the cusp behaviour (Kato 1957) in orbital-free density functional theory with standard kinetic energy functionals, by the introduction of a physically-motivated cost functional. He showed that in this way the electron density, it gradient and Lapla-

can be nearly exact in the vicinity of nuclei, and shell structure emerges. This results in significantly reduced energy errors and provides a foundation for the development of next-generation kinetic energy functionals (Lehtomäki 2019, 2019).

Prof. Ayers of McMaster University spoke about nontraditional resummation methods that are well-adapted to strongly divergent gradient expansions and discussed their performance. He stressed that some constraints on the kinetic energy functional may help explain why the problem of kinetic energy functionals appears to be extremely difficult, while providing guidance for future investigations.

Prof. Olga Lopez-Acevedo from Universidad de Antioquia showed how large-Z (large ionic charge) limit can be a useful concept for the development of kinetic energy functionals. In particular, she showed that the use of an exact constraint coming from semiclassical physics allows avoiding empirical parameters of electron density gradient-based kinetic density orbital-free functionals. This method of parametrization is general enough so that it could be applied to parametrize kinetic functionals based on higher derivatives of the electronic density.

Recent developments of non-local *free energy* density functionals at Jilin University were presented by Cheng Ma. Such functionals are needed in particular for the simulations of warm dense matter i.e. many applications ranging from simulations of heat treatment to melts to nuclear fusion.

Dr. Kai Luo from Nanjing University of Science and Technology spoke about latest research on semilocal kinetic functionals and presented a new KEF, an augmented variant of Perdew-Constantin functional (Perdew 2007, Wang 2024).

Prof. Mi from Jilin University overviewed recent developments in KEDF (kinetic energy density functional) and local pseudopotential development at Jilin University, innovations that have significantly broadened the range of applicability of OF-DFT, enabling successful simulations of more complex systems beyond simple metals, such as semiconductors and quantum dots (Mi 2023, Xu 2024).

Dr. Della Sala from the Italian CNR-IMM presented recent advances in Quantum-Hydrodynamic Theory (QHT) – an orbital-free approach that allows one to compute the absorption spectrum directly from the ground-state density (Ciraci 2016, Baghranyan 2021), an alternative to the orbitals-dependent time-dependent (TD) DFT used for that purpose with KS DFT.

An alternative approach to OF-DFT was presented by Dr. Martin Trappe of National University of Singapore: Orbital-Free Density-Potential Functional Theory (DPFT), where the variational variables are both the density and an effective potential, with expressions built on systematic Suzuki-Trotter factorizations of the quantum-mechanical propagator and on the Wigner function formalism, to derive nonlocal as well as semilocal functional approximations without resorting to system-specific approximations or ad hoc measures. Dr. Trapper presented first applications of the method to real-world systems such as metal nanoparticles.

## 2. Developments in OF DFT software,

Liang Sun from Peking university introduced to the attendees the ABACUS code, an open-source ab initio computational package with OF DFT implementation.

Cheng Ma of Jilin University presented implementation in the ATLAS (Mi 2016) software of a free-energy functional for warm dense matter simulations.

Prof. Pavanello introduced the DFTpy code, a Python implementation with OF-DFT and TD OF-DFT capability (Shao 2021).

3. Developments in applications of data-driven methods and machine learning to the construction of both the KEF and LPPs and for property prediction.

Several talks presented advances in machine-learned KEFs:

Liang Sun from Peking University presented a novel ML-based physical-constrained non-local KEDF (MPN KEDF).

Prof. Rincon from Universidad San Francisco de Quito in Ecuador presented semi-local KEFs using Kolmogorov-Arnold networks.

Prof. Manzhos from Tokyo Tech presented a machine-learned orbital free KEF that uses gradient expansion based features and accurately reproduces energy-volume curves of hundreds of unary, binary and ternary compounds.

Prof. Cardenas from Universidad de Chile presented deep neural network based machine learning of Kohn-Sham kinetic energy density. They have used different functionals of the density as input features of the NN, including a set of non-local descriptors inspired in the electron delocalization range function by Janesko et al., which have shown to notably improve the results, based on applications to synthetic systems.

Prof. von Rudorff from University of Kassel presented how Alchemical Perturbation Density Functional Theory (APDFT) (von Rudorff 2020) – a method for exploration of chemical space and discovery of new materials with desired properties – can be used with OF-DFT.

Prof. Luder from National Sun Yat-sen University addressed the problem of data availability when doing machine learning based OF-DFT development, whereby existing materials databases provide structural and property information but not the data on which for example KEFs can be trained. He presented first development towards an a OF-DFT targeted database containing gridded data of electron density and density-dependent quantities of hundreds of unary, binary, and ternary compounds.

Prof. Pengwei Zhao from Peking University spoke about machine learning for Orbital-Free Density Functional Theory *for atomic nuclei*, where one machine-learns the kinetic energy as a functional of the nucleon density alone. DFT for nuclei has evolved into a separate field from traditional DFT applications to molecules and solid materials. In that field too researchers explore orbital-free functionals of electron density including KEFs. This presentation helped connect the conference to this field with which we really interact but which deals with many similar issues, so more interactions are desired (Yang 2021, Wu 2022).

Dr. Alberto Vela from the Mexican Cinvestav-Zacatenco presented the application of machine learning, specifically neural networks, to conformational analysis and molecular assembly and to the calculation of chemical descriptors derived or justified within Conceptual-DFT.

Dr. Zhao from Yunnan University presented a deep learning approach for simultaneous prediction of polarizabilities and NMR shieldings of macromolecules and their aggregates with the help of linear-scaling generalized energy-based fragmentation (GEBF) method (Zhao 2023, 2023, 2024).

4. Recent developments in electron density based topology analysis techniques and in density-based analysis of phenomena, as well as developments of electron density based models that are effectively hybrid approaches between OF DFT and force fields.

KEFs are functionals of electron density based quantities; Prof. Matta from Mount Saint Vincent University in Canada spoke of latest advancement in QTAIM-based (quantum theory of atoms-in-molecules) (Bader 1990) electron density-based descriptors, in particular electron localization-delocalization matrices (LDM) (Matta 2024). LDMs are a bridge between quantum chemistry and chemical graph theory and have been found to be powerful predictors of molecular properties as diverse as pKa, boiling points, substituent effects,

aromaticity, corrosion inhibitor activity (including the discovery of active species), mosquito repellency, absorption properties, enzyme catalysis, etc. They are of interest as potential descriptors for OF-DFT functional construction as well as for materials informatics.

Prof. Popelier from University of Manchester presented a force field where the energy calculation is based on an electron density representation and the so-called "quantum atom" defined in QTAIM. As the energy is effectively computed from the density (Popelier 2015, Manchev 2024) this can be viewed as a hybrid between OF-DFT and a force field as a function of atomic coordinates.

Prof. Chunying Rong of Hunan Normal University spoke about development and applications of the density-based theory of chemical reactivity, an electron density-based conceptual framework to appreciate physicochemical properties. She provide an overview of ways to tackle the matter, including orbital-free density functional theory, conceptual density functional theory, direct use of density-associated quantities, and the information-theoretic approach. She highlighted several recent advances to realize new understanding of chemical concepts such as covalent bonding, noncovalent interactions, cooperation, frustration, electrophilicity, nucleophilicity, regioselectivity, and stereoselectivity (Rong 2022, He 2024).

Prof. Julia Contreras-Garcia from Sorbonne spoke about obtaining insight into phenomena such as electronic organization and superconductivity from the analysis of kinetic energy density (Belli 2021, di Mauro 2024).

#### 5. Related developments in other large-scale electronic structure methods.

Several presentations concerned with large-scale DFT based calculations with approached other than OF-DFT:

Dr. William Dawson of the Japanese RIKEN presented the theory and implementation aspects of order-N DFT in BigDFT code (Ratcliff 2020). Some of the algorithmic solutions developed in this research such as those pertaining to optimization problems or electron density representation could be deployed also for OF-DFT advancement.

Yongshuo Chen from Jilin University presented the development of a new scheme for reconstructing of kinetic energy density functionals (KEDFs) using the tight-binding approximation, creating an interesting and promising connection to the semi-empirical DFTB (density functional tight binding) (Hourahine 2020) method.

Prof. Shengjun Yuan from Wuhan University presented large-scale ab initio methods based on wave propagation that abandon the explicit expression of eigenstates or orbitals (calculations of which are major contributors to the cost of KS DFT) but benefit from the random state propagation in real space. They transform the problems of solving the stationary Schrödinger equation to the time-dependent Schrödinger equation, thereby circumventing the need for diagonalization and thus enabling large-scale ab initio calculations.

Dr. Hu from University of Science and Technology of China presented the discontinuous Galerkin Hartree-Fock method and showed its ability to predict accurate electronic structures of complex metallic systems with millions of atoms - the scale vied for by OF-DFT.

Prof. Ke from ShanghaiTech University presented the random orbital based Green's function method capable of handling tens of thousands of atoms and its applications large-scale material and device modeling (Tang 2024).

#### 6. Applications in need of OF-DFT.

Prof. Kulbir Ghuman of the Canadian INRS spoke from the perspective of applied computational materials

science. She presented an overview of research problems specifically faced by researchers doing materials modeling for renewable energy technologies where the intrinsically large-scale nature of phenomena, as well as lack of reliable force fields, call for large-scale electronic structure methods, including some applications where even order-N KS DFT is of limited applicability and where OF-DFT capabilities are desired, as models with millions of atoms are involved. These include grain boundaries and other interfaces, disordered materials, defect segregation and other phenomena important for batteries, fuel cells, and elsewhere.

Dr. Trappe highlighted in his talk on DPFT the need for direct ab initio modeling of nanoparticles and presented first adaptation of th DPFT method for this application.

Prof. Pavanello highlighted in his talk the need for large-scale DFT capabilities, now provided by time-dependent OF-DFT that he gave birth to, for the modeling of plasmonic properties of nanoscale materials where KS DFT methods are unwieldy.

Prof. Manzhos in his presentation highlighted the need for, and in some cases an already existing availability of, OF-DFT capabilities to model mechanical properties including plasticity and fracture of alloys. He also showcased the pitfalls of force-field based modeling currently applied for these purposes and how OF-DFT can address them in substance.

## 4 Scientific Progress and Outcome of the Meeting

One of the results of the meeting was that our scientific program made connections among various sub-fields related to orbital-free DFT and to large-scale DFT methods in general, and related algorithmics and applications. There were robust interactions among researchers representing these sub-fields, which resulted in plans for collaborations and mutual grant applications. While scheduled discussion sessions were helpful in this, a lot of informal interactions happened during joint meals, breaks as well as outside the workshop.

While I cannot speak in detail for other participants, this was in particular the case for me and several participants with whom we made follow-up plans. The true impact of the meeting will start appearing in 2+ years which is approximately the lead time after which concrete results (papers, presentations, grants) may begin to appear.

We had a number of non-presenting attendees, including young researchers who are still new to OF-DFT. They learned about the method or rather the collection of methods involved, about key issues where they could make an impact, and about applications where OF-DFT can be deployed already now or is expected to become applications-ready in near future.

As OF-DFT as a method nears applicability to many research problems, it is important to inform a large pool of researchers about it and involve some of them in it, focusing on younger researchers who will be the future of OF-DFT based computational materials science. With this workshop, We made a (necessarily) small step in that direction.

## 5 Acknowledgements

The organizing committee are grateful to the local IASM - Zhejiang University team in Hangzhou for perfect organization. Everything was taken care of so that the organizers and the attendees could focus only on science. We are happy to have chosen IASM as our first-choice location.

We have experienced firsthand just how useful BIRS is for organizers and how important it is for the promotion of international scientific collaboration, and they are thanked for this important work.

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