# Understanding and discovering materials *in silico*

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Materials are at the heart of technology, and to large extent technological progress depends of finding materials with superior or previously unknown properties. Search for such new materials is a vast domain of research in physics, chemistry and materials science, and the range of problems considered is very broad. For instance, one may look for more efficient materials for solar cells or materials that would make quantum computers our everyday reality. My research aims at discovering new materials and properties "*in silico*", that is by performing computer simulations as opposed to the traditional experimental research. Recent developments in computer hardware, algorithms and theoretical formalisms allow performing *in silico* predictions of physical properties of materials orders of magnitude faster and cheaper as compared to carrying out equivalent experiments. On the other hand, we have to pay the price of dealing with an extra uncertainty in our *in silico* predictions because a large number of approximations have to be introduced when describing physical reality on computer. A material discovered on computer we call a "candidate material", and it becomes the real discovery only once confirmed by experiments.

Below, I would like to present several such *in silico* predictions made by me and my group that received experimental confirmation.

**Magnetic graphene nanomaterials**

Early in my career, I have made a series of highly regarded contributions in the field of magnetism in materials made of carbon. This research activity started as a purely curiosity-driven project while I was completing my PhD thesis on an unrelated subject. At that time, the subject of graphene, the first truly two-dimensional material, has just started and was developing very quickly. But already in 2010 the discovery of this one-atom-thick material was recognized by the Novel Prize in physics. My first contribution in this field was the theory of defect-induced magnetism in graphene introduced in Ref. [Yazyev07], and further developed in Ref. [Yazyev08a]. The proposed physical mechanism relates the onset of magnetic ordering to the magnetic instability of the quasilocalized states that result from breaking the local bipartite symmetry of graphene lattice by point defects, such as vacancies or hydrogen chemisorption (Figure 1a,b). Importantly, both ferromagnetic and antiferromagnetic correlations can be realized in graphene-based systems depending on the distribution of defects between the two sublattices. These two papers explained the puzzling observations of ferromagnetism in proton-irradiated graphite, and most importantly, provided crucial understanding that stimulated research towards possible technological applications of magnetic graphene nanostructures. The theory received a series of experimental confirmations, with the most direct one from scanning probe microscopy being reported almost after a decade following (Figure 1c,d) [González-Herrero16]. I'm also responsible for several important works on edge magnetism in graphene, a popular research direction that started around twenty years ago producing an astonishing number of theoretical works with little experimental evidence, until recently. In particular, I have published a theoretical study of spin correlations at graphene edges,

thus highlighting the challenges of experimental detection of this exotic type of magnetism and establishing its limitations for practical applications [Yazyev08b]. Furthermore, I have made a critical theoretical contribution to the first experimental confirmation of edge magnetism in graphene by means of scanning probe microscopy [Tao11]. This experimental work was followed in a publication on the theory of magnetic edge states at chiral graphene edges [Yazyev11]. Jointly with my colleagues at Harvard, I have developed a theory that allowed designing magnetic interactions in graphene-like molecules [Wang09]. Once again, our prediction received an experimental confirmation [Mishra20]. Overall, the research direction of magnetic graphene systems was summarized in a review article that presented a single generalizing viewpoint on magnetism in graphene-based systems of different dimensionalities [Yazyev10a]. This review has made a significant impact in the community and was recognized by a large number of citations.

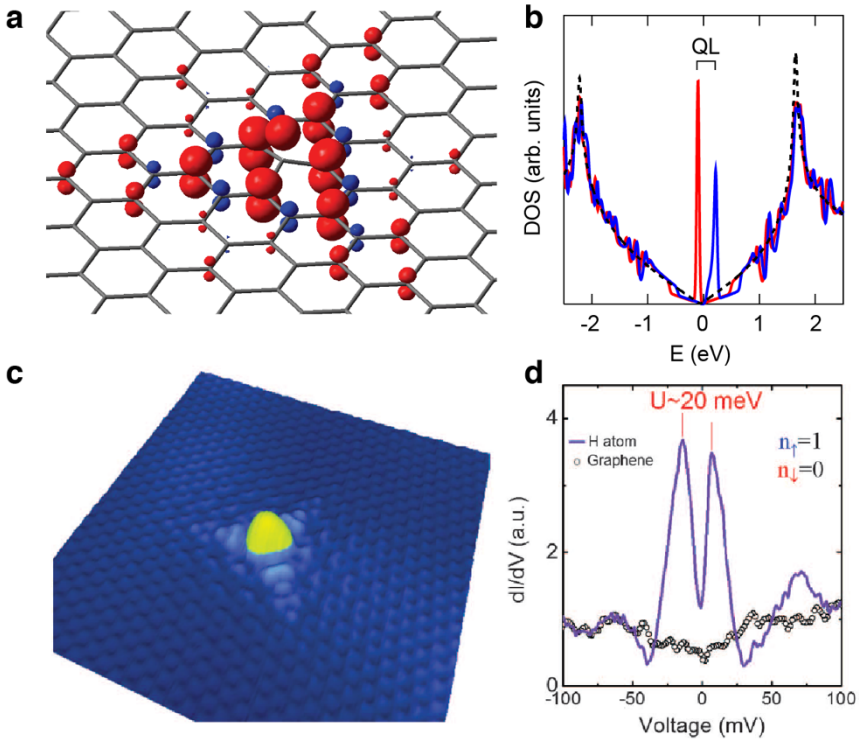


**Figure 1.** (a) Spatial distribution of the quasilocalized state at the hydrogen chemisorption defect in graphene and (b) the corresponding spin-resolved density of states as predicted by theory presented in Ref. [Yazyev07]. Reproduced from Ref. [Yazyev10]. (c) Scanning tunneling microscopy image of the quasilocalized state at the hydrogen chemisorption defect and (d) the corresponding experimental *dI*/*dV* curve showing the predicted spin splitting. Reproduced from Ref. [González-Herrero16].

## Topological defects in graphene and other two-dimensional materials

I have made pioneering predictions of the structure and basic thermodynamic properties of topological defects in graphene – dislocations and grain boundaries (Figure 2a) [Yazyev10b]. Such defects are intrinsic to polycrystalline morphologies, and hence are practically unavoidable in sufficiently large, beyond-micrometer scale samples of two-dimensional materials that are very susceptible to disorder. This work

established the foundations for understanding a wide range of properties of polycrystalline two-dimensional materials. The predictions regarding the structure of topological defects have soon received full experimental confirmation (Figure 2b,c), see e.g. Ref. [Huang11]. My further activity in this quickly evolving area of research focused on understanding the electronic transport phenomena in polycrystalline two-dimensional materials. This problem was identified as especially important due to the fact that the most appealing technological applications of two-dimensional materials are believed to be in the domain of electronics, while topological defects would certainly have very strong and complex effects on the characteristics of electronic devices based on such two-dimensional materials. My first publication along this direction established the role of momentum conservation in the electronic transmission across the periodic grain boundaries in graphene [Yazyev10c]. Importantly, the work also proposed a conceptually new type of graphene-based electronic devices that exploit transport gaps resulting from momentum conservation instead of traditionally considered engineered band gaps. The two abovementioned works were proposed and realized within the Swiss NSF postdoctoral fellowship project carried out at University of California, Berkeley in the group of Steven Louie. After starting my own independent research group supported by the Swiss National Science Foundation Professeur Boursier fellowship, I have made several other important contributions along this direction, including the equivalence of isolated dislocations in graphene to resonant scattering centers [Gargiulo14], investigation of valley- and spin-filtering phenomena in graphene [Chen14] and transition metal dichalcogenides [Pulkin16], joint experiment-theory observation of the buckling transition at grain boundaries in graphene [Tison14]. Current developments of this direction of research are summarized in his recent review article [Yazyev14].

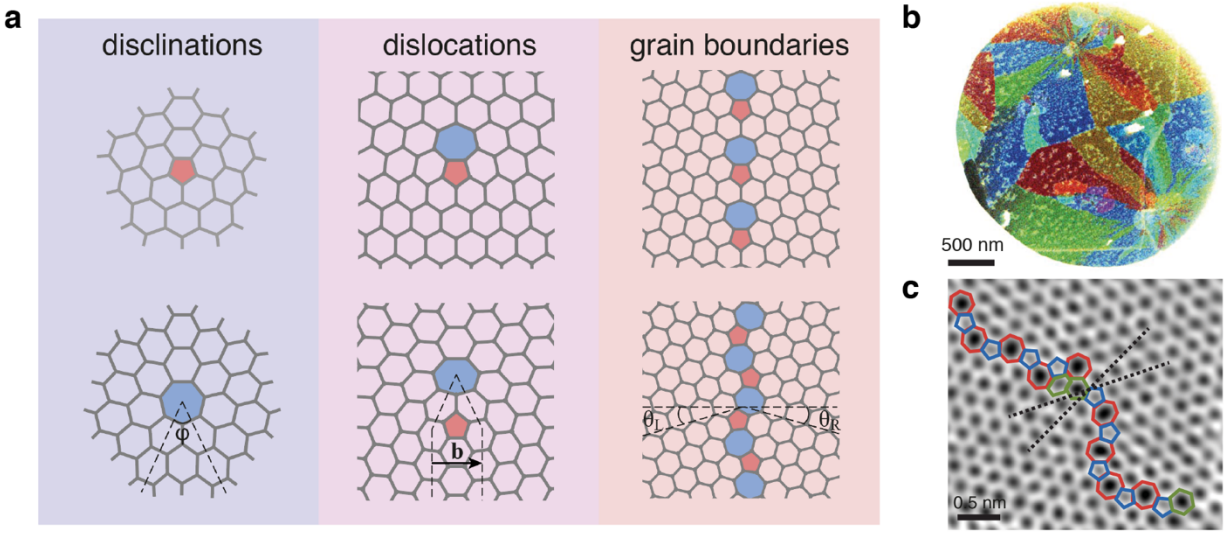


**Figure 2.** (a) Atomic structure and hierarchical relations of three types of topological defects in polycrystalline graphene – disclinations, dislocations and grain boundaries. Reproduced from Ref. [Yazyev14]. (b,c) Transmission electron microscopy images of graphene grown by chemical deposition showing polycrystalline morphology at micrometer length scales (panel b) and atomic structure of a representative grain boundary (panel c) fully consistent with the theoretical model of Ref. [Yazyev10b]. Panels b and c reproduced from Ref. [Huang11].

**Discovery of novel materials realizing topological phases**

My interest in topological aspects in physics has naturally resulted in an involvement in the nascent field of topological materials. I was among the first to investigate the reference bismuth chalcogenide topological insulators using first-principles calculations, both at the level of density functional theory [Yazyev10d] and many-body perturbation theory techniques [Yazyev12]. Major efforts in this field are currently dedicated to the search of novel materials realizing a variety of topological phases (topological insulators, Dirac and Weyl semimetals, nodal-line metals, etc.). Very recently, my group has developed a framework for the high-throughput computational search of topological phases among known crystal structures (Figure 3a) described in publicly available sources such as the International Crystal Structure Database (ICSD). This initiative was supported by the national project NCCR Marvel on computational materials discovery and the European Research Council Starting grant that I obtained in 2012. The first successful application was the discovery of a novel topological phase in the quasi-one-dimensional bismuth iodide (Figures 3b-e) [Autès16a]. A number of properties distinguish this material from other currently known topological insulators, including the high anisotropy of the Dirac fermion surface states, low density of bulk charge carriers, etc. Moreover, it now appears that this is just the first representative of an entire new family of bismuth halide topological materials. The theoretical prediction of the topological phase in $\beta$-$Bi_4I_4$ done by my postdoc Dr. Gabriel Autès received full confirmation that required participation of a large number of experimental groups. All these results reported in one single paper (Ref. [Autès16a]) illustrate the full cycle of materials discovery, starting from theoretical prediction to materials synthesis and photoemission experiments that reveal the topological insulator phase. Among other achievements in this direction one can also mention the prediction of robust type-II Weyl semimetal phase in Mo and W diphosphides [Autès16b]. Soon after our prediction, a large number of experimental groups reported truly extraordinary properties of $WP_2$ making it a “rising star” material in the condensed matter physics community. In particular, $WP_2$ was identified as material with very high low-temperature conductivity, extremely large residual resistivity ratio (highest known among binary materials) and exceptionally large magnetoresistance (200 million percent at 63 T and 0.5 K) [Kumar17], hydrodynamic electron fluid transport [Gooth18] and even a claim for observing negative resistivities [Lv17]. Many other exciting materials identified in my group are currently being considered. What is important, we have made the entire set of data resulting from our high-throughput search for new topological materials publicly available. The database with the results can be freely accessed on the Materials Cloud web portal (https://www.materialscloud.org/discover/topomat).

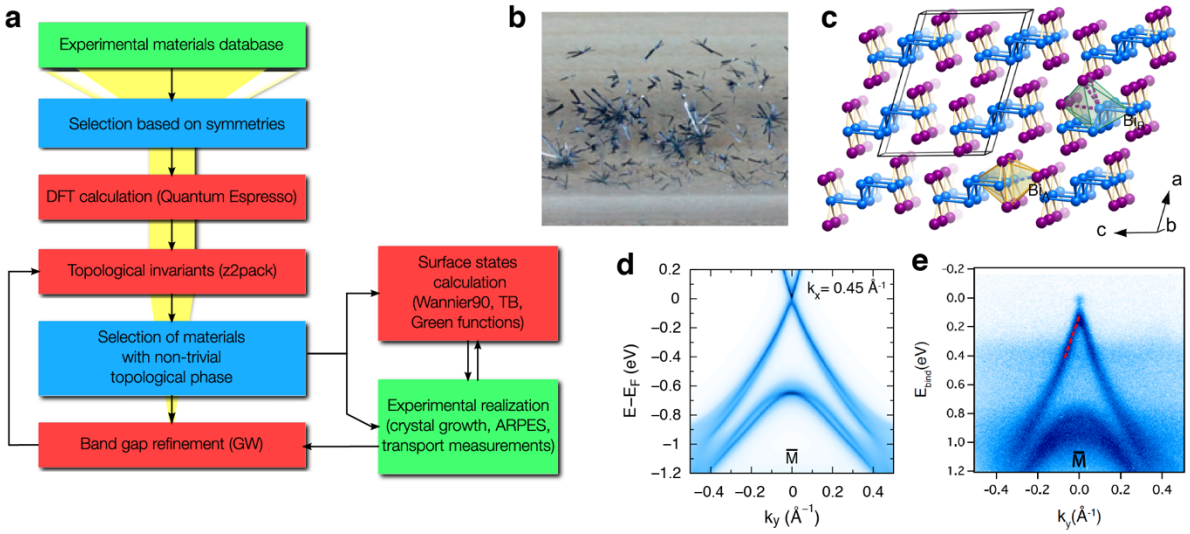


**Figure 3.** (a) Schematic representation of the high-throughput search workflow for the discovery of novel topological materials. (b) Sample morphology and (c) crystal structure of the discovered $\beta$-$Bi_4I_4$ topological insulator. (d) Theoretically predicted surface local density of states and (e) experimentally measured angle-resolved photoemission intensity for the (001) surface of $\beta$-$Bi_4I_4$. The two sets of data agree well with each other. Panels b-e reproduced from Ref. [Autès16a].

## Research plans and vision

Starting with a focus on one particular material – graphene – my research program of was constantly extending to include other materials simply following my scientist's curiosity. By now, materials discovery has become the major component of my group's activity. The research program is currently evolving in the following two directions. Firstly, the expertise in high-throughput computational search of novel materials and the developed methodological framework are great assets to attempt solving other important problems in materials discovery. In short term, my team is pursuing the search of novel skyrmion materials, a new class of magnetic materials that are interesting from the point of view of prospective applications in information technology. This research is realized within the SNSF Sinergia collaborative project that involves several other groups in Switzerland. Another highly ambitious goal is the search for the first material realizing the Kitaev model, an exotic spin liquid phase that has Majorana fermion elementary excitations and promises a robust platform for topological quantum computing. Secondly, from the search among previously synthesized materials I plan extending the scope of my activity to materials design, that is the realization of materials that have never been made before. Solving this intrinsically more complex problem will greatly extend the reach of computational materials discovery. I'm especially attracted by the possibility of designing materials for clean energy applications, since this research addresses one of the immediate challenges that the humanity is currently facing. I hope my research will make a sizable contribution towards the sustainable future of our home planet.

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