Project Title:

High-temperature superconductivity by quantum Monte Carlo: the iron-chalcogenides family

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1. Background and purpose of the project, relationship of the project with other projects

The discovery of the iron-based high-temperature superconductors (FeSCs) in 2008, after about 20 years from the first discovery of high-temperature superconductivity (HT_c) in the cuprate family, has provided further evidence that a new theoretical framework is unavoidable to understand this effect. Therefore it is extremely important to develop new simulation techniques in order to reproduce the present experimental results, with the final very ambitious goal of predicting, simply by computer simulation, novel superconducting materials for potential commercial applications.

In this project, we plan to use an advanced ab initio many-body technique based on quantum Monte Carlo (QMC) and a highly accurate variational wave function. By means of our approach, rather different from the conventional DFT or GW paradigm for ab initio simulations, we are going to study systematically few materials in the iron chalcognides (Se,Te,S). They show a simpler geometrical structure with respect to iron pnictides, but at the same time they retain all the interesting properties of other FeSCs; this peculiarity makes chalcogenides a perfect laboratory for studying unconventional superconductivity, both theoretically and experimentally.

A particular attention will be focused on the iron selenide (FeSe), and the connection between its structural properties and superconductivity. Parallel to this study, we plan to develop a widely used technique to reduce the size effects based on k-sampling and allow affordable but still reliable calculations with much smaller number of atoms. The generalization of this technique to superconducting wave function is not straightforward but we think it is possible and will be particularly useful in this project.

2. Specific usage status of the system and calculation method

We used mainly the massive parallel computer (MPC) for production runs, while we used the application computing server (ACS) for postprocessing analysis. Porting our code on both machines has been very straightforward, and we exploited the compatibility option between the binary files generated by the starc executable and those produced by the intel based compiler run on the ACS machine. We found this a great and unique feature of Hokusai great-wave. Running on Hokusai has been always smooth, however we found a quite long waiting time in the queue, which justifies our usage of 47% of the total budget on Feb. 19th. We are aware that this has been a common problem affecting other users as well. The disk usage has been pretty intensive (3 TB occupied on Feb. 19th), which is related to the need of storing Monte Carlo configurations to compute correlation functions and other observables after the variational and diffusion MC runs.

3. Results

We carried out QMC calculations on bulk FeSe with the widely used Jastrow-Slater many-body wave function as variational ansatz. Magnetic order is obtained by constraining the determinant orbitals to have the desired spin pattern.

Thanks to a unique feature of our approach, we have been able to obtain the QMC relaxed structure of FeSe at different magnetic configurations as well as in the paramagnetic phase. We found that QMC improves previous DFT results

on both cell and internal parameters, attaining a close agreement with the latest experimental works in the collinear configuration. The same agreement is shown by bulk modulus calculations.

Due to its importance for superconducting properties, a particular attention has been devoted to the Se height (hSe) over the iron planes. By performing calculations at pressures ranging from 0 GPa to 8 GPa, we found that also in the case of hSe QMC results in the collinear phase are in good accordance with the experimental trend, although the experimental points are quite scattered, depending on the experimental dataset.

It is established that hSe is also a very sensitive parameter in determining the relative energetics among different magnetic orderings. By selecting the QMC relaxed value of hSe, we perform an extensive investigation of the energetics of FeSe with several magnetic configurations: collinear, bicollinear, collinear with defects, simple antiferromagnetic (checkerboard), ferromagnetic and staggered dimer. First of all, the collinear configuration, which gives the best agreement with experiments for structural parameters and bulk modulus, turns out also to be the ground state over the whole considered pressure range. This outcome is at variance with DFT-PBE where the ground state is always the staggered dimer phase. The DFT picture is improved by using the hybrid functional PBE0 approach; however, while energetics is in closer agreement with QMC, the metallic properties of FeSe cannot be captured by DFT-PBE0 which shows instead a rather large band gap.

Another important feature of QMC energetics which is not taken into account by less correlated methods as DFT is that the magnetic configurations containing spin chains (collinear-like configurations) tend to converge in energy as pressure is increased, whereas non collinear phases, such as checkerboard or ferromagnetic, tend to diverge as pressure gets higher with respect to the ground state. The crossing point between the several collinear states we considered is found around 8 GPa, thus very close to the pressure displaying the highest critical temperature. By relying on fully *ab-initio* calculations, this result shows an intriguing connection between collinear spin fluctuations and superconductivity, which has been actually spotted experimentally.

A careful investigation of the electron charge variance allowed us to give a simple explanation of this behavior. In particular, we found that the spin minority - the down spins in an atom containing majority of up spins and viceversa – is highly delocalized and therefore it mostly contributes to magnetism within FeSe. The delocalization is also affected by the magnetic orders and collinear-like phases show a larger degree of delocalization with respect to non-collinear ones. This accounts for the aforementioned FeSe energetics. Indeed, spin minority electrons require at least a parallel neighbor in order to hop to another atom, thus disfavoring ferromagnetic and antiferromagnetic pattern. This mechanism is in competition with the interaction among the large Fe magnetic moments (~3.1-3.4 μ_B) and the resulting compromise is a collinear pattern which includes both parallel and antiparallel spin configurations and it is energetically favored.

The above results have been obtained by a joint collaboration with a theoretical group in Urbana-Champaign (Illinois), aimed at validating the outcome by using two different schemes of wave function optimization. The one implemented in the code we used (TurboRVB) is based on a direct and flexible optimization of the wave function parameters, while the one used by the Urbana group tunes the exact exchange fraction in DFT to generate the optimal orbitals to be used in QMC. We found a perfect match between the results, which validate and strengthen the final outcome on FeSe provided by QMC.

Concerning the second part of the project, we successfully carried out the implementation of the twist-average technique for reducing finite size effects. This upgrade required also a relevant methodological development of our code in order to include the necessary formalism for dealing with complex variational wave functions. We also devised a simple but original procedure to compute special k-points for effectively reducing the finite-size error within supercell simulations. This procedure has efficiency comparable to the more expensive twist-average technique by using only one twist value. This will be the subject of a future publication.

The code improvements carried out during this project will be of paramount importance for extracting pairing functions

and superconducting properties of single-layer FeSe, which is the subject of a project proposal we submitted for the following fiscal year.

4. Conclusion

We achieved an accurate description of the magnetic short-range correlations of FeSe as they develop under pressure. By performing many-body quantum Monte Carlo simulations from first principles, we clarified the role of the Se height to stabilize collinear magnetic configurations, whose order is in stark contrast with density functional theory calculations based on the popular PBE functional. Improvement is found by using a hybrid functional such as PBE0, which reproduces together with QMC the experimental structural properties (crystal parameters and bulk modulus) for its lowest energy state, which shows collinear spin order. However, only QMC seems to be able to account for the metallic properties of the compound in the phase with strong collinear spin fluctuations. An intriguing picture, which emerges from our QMC results, is that there is a collapse of different collinear phases (collinear, bicollinear, collinear with defects) as the pressure increases, suggesting the importance of degenerate spin configurations with strong (0,pi) fluctuations to enhance the superconducting critical temperature. The FeSe monolayer could show an even stronger interplay between geometry and spin fluctuations, in light of its high critical superconducting temperature, which deserves a farther deep investigation, with the tools developed along this project.

5. Schedule and prospect for the future

We submitted a new project for the next fiscal year, which includes a detailed description of the perspectives of the present one, and the scheduled tasks of the new project. Our interest is mainly focused to understand the physical properties of the FeSe monolayer, which shows a record Tc of about 100 K, and is promising for engineering even higher Tcs, via a controlled growth and doping of the monolayer. The appealing features of our approach are the controlled finite size scaling thanks to an improved k-point sampling and the possibility to optimize directly the pairing function, and so detect a possible superconducting instability enhanced or induced by strong electron correlation and spin fluctuations.

6. If no job was executed, specify the reason

We refer the reader to Section 2, which explains our usage of the allocated resources. In fact, we have been able to run a large enough number of jobs to reach part of the goals of the 2015 project.

Fiscal Year 2015 List of Publications Resulting from the Use of the supercomputer

[Oral presentation at an international symposium]

French meeting of GdR-Mico (http://gdr-mico.cnrs.fr/spip.php?rubrique132), contributed talk, "Improper s-wave symmetry of the electronic pairing in iron-based superconductors from ab-initio quantum Monte Carlo calculations'' by Michele Casula, Nov 23-25 2015, Paris

[Others (Press release, Science lecture for the public)]

Brian Busemeyer, Mario Dagrada, Sandro Sorella, Michele Casula, and Lucas K. Wagner, "Competing collinear magnetic structures in superconducting FeSe by first principles quantum Monte Carlo calculations", preprint (arXiv:1602.02054).