Prof. David Gross, Director
Kavli Institute for Theoretical Physics
University of California, Santa Barbara
Santa Barbara, CA 93106

Dear Prof. Gross,

hereby we propose a KITP program named *Ab-initio approaches to excitations in condensed matter: from basic concepts to complex interactions in materials*, which should be held in the winter semester 2009/10. A description of the scientific background, the aims of the program, and the planned activities are given below.

Sincerely,

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Ab-initio approaches to excitations in condensed matter: from basic concepts to complex interactions in materials

Materials Science requires a qualitative and quantitative description of processes taking place on the atomic scale. In this context electronic-structure theory is the first level in the hierarchical set of models needed to quantitatively describe and understand phenomena that are seen in condensed matter and the function of real materials. For polyatomic systems, density-functional theory (DFT) with present-day exchange-correlation functionals has proven to be an excellent technique for the calculation of structures and molecular dynamics. However, it is not as good for certain types of interactions. Accurate treatment of strong electronic correlations, hydrogen bonding, van der Waals interaction, and molecular dynamics of electronically excited states, nonadiabaticity and transport represent the first (and severely) broken links in the chain of modeling, and therefore are major current research priorities. Improvements are not only important, but crucial.

If electronic-structure theory can be developed to the point of giving quantitative predictions, then this accuracy can and should be propagated up the chain of methods to successively increasing spatial and temporal scales. Then, and only then, each level of modeling would yield predictions that can be used in the rational design of functional materials. The present long-term KITP program concentrates on this

base always having in mind the relevance for the description of real functional materials.

The electronic excitations governing the performance of opto-electronic devices, electronic relaxation processes on semiconductor surfaces and interfaces, the electron dynamics at metal surfaces, the prediction of new materials for batteries or temperature-resistant, lightweight, and ductile alloys for applications in the energy, automotive and aviation industries are just a few out of the manifold topics, which all ask for a profound understanding of the underlying physics and for reliable and highly-precise numerical first-principles methods at the same time.

The tremendously improved resolution of experimental methods during the last decade as well as the functionality of materials sensitively depending on complex interactions pose a challenge to advances in theory. Hence both, the academic interest in basic physics and the need for applied research, drive the development of condensed matter physics and computational materials science.

When several processes happen on a comparable energetic scale, complex interactions may take place, which require a unified treatment. While great progress has been achieved in the different areas, like in manybody perturbation theory (MBPT), time-dependent density functional theory (TDDFT), electron-phonon coupling and superconductivity, *ab-initio* molecular dynamics, first-principles approaches to chemical reactions, and, last but not least, in density-functional theory itself, the combination of the different areas is still a challenging task. For example, electronic excitations in organic semiconductors can be handled nowadays within MBPT by solving the Bethe-Salpeter Equation. At the same time experimental spectra exhibit phonon replica, which at present cannot be treated within the same theoretical framework. For the calculation of transport properties, usually only the electronic states are computed from first principles, while the scattering processes and the quasiparticle lifetimes determining e.g. the electrical conductivity and other properties, are often treated with simple models like a constant life-time broadening. Only recently, the detailed knowledge of the phonon band structure has entered the computation of thermo-elastic properties from first principles.

The aim of this KITP program is to survey the state-of-the-art and recent achievements in the single research areas, to discuss their future perspectives, and to put forward new approaches in interrelating these fields with each other.

The most important topics are:

Electronic excitations: State-of-the-art methods to describe electronic excitations are MBPT (the *GW* approach combined with the solution of the Bethe-Salpeter Equation) and time-dependent DFT. While the former is a Green function approach to many-body theory making use of DFT (or alternative) ground state calculations, TDDFT represents a natural extension of DFT to time-dependent excitations. Despite the success of both routes, many open questions remain, which are hot topics in solid state research. Examples are the self-consistent (or not) *GW*, and quantitative

discrepancies between all-electron and pseudopotential results for various properties. Concerning TDDFT, the search for reliable xc kernels, and the question on whether one can construct kernels that are independent on a preceding *GW* run, are essential for the applicability of this approach to a wide range of materials.

Electron-phonon coupling: Superconductivity in many metallic systems is the most striking evidence of the importance of electron-phonon (*ep*) coupling. Issues such as electron renormalization due to *ep* interaction, and phonon lifetimes are hardly tackled so far, but can generally be treated within MBPT. To which extent, in turn, these affect the critical temperature in superconductors remains a completely open question. Superconductivity in low-dimensional nanostructures like intercalated graphite and graphene-based borides is another exciting topic. There are, however, many other examples where *ep* interaction plays a crucial role. Being strongly enhanced in low dimensions, it governs electronic relaxation processes on semiconductor surfaces and interfaces, and determines the electron dynamics at metal surfaces through a competition between *ep* coupling and electron transport. Concerning chemical reactions, there is growing experimental evidence that many dynamic processes at surfaces are non-adiabatic, i.e., electronic excited states play an important role. Non-adiabatic electronic excitations in photo-activated processes is another topical issue in bio-materials.

Electron and ion transport: The last decade has witnessed a renewal of interest in electron transport processes driven by the emergence of nanoscience and advances in nanofabrication. At the nanoscale, transport requires a full quantum mechanical treatment, which is particularly challenging for out-of-equilibrium phenomena like transport. Several theoretical approaches have been developed: linear-response formulations, valid at low bias, as well as schemes like the non-equilibrium Green's function (NEGF), the Lippman-Schwinger equation, and the master equation, which are valid also beyond the linear regime. So far, most calculations have been based on ground state DFT but a number of questions on the viability of this approach to transport have been raised, because transport actually probes low lying excitations. Moreover the transport characteristics of devices coupling molecular structures, especially organic molecules, to metallic electrodes crucially depend on the alignment of the molecular levels with the metallic Fermi level. This alignment is often not very well described by the Kohn-Sham levels of DFT. How to solve these difficulties, whether by TDDFT, by MBPT, or, more simply, by self-interaction corrected DFT schemes such as LDA+*U*, is a matter of current debate and ongoing research. Another issue concerns the interplay between dissipative and ballistic transport phenomena. Although transport through nano-junctions is predominantly ballistic, experimental evidence of dissipative phonon scattering and Joule heating has been collected in various circumstances, raising the issue of how to include phonons in addition to electrons in transport theories and how to deal in general with dissipative phenomena and open quantum systems. Due to the many challenges associated to electron transport at the nanoscale aggravated by the hype on

molecular electronics devices, the field has been plagued since the beginning by experimental and theoretical difficulties. For instance, some initial experimental claims have been subsequently dismissed due to severe problems in controlling the experimental setup and confidently reproducing the data. Similarly, some theoretical results relied on models that were too crude to have a real predictive value. Recently, the situation has significantly improved with major advances in both, experimental and theoretical sides. Thus the time is ripe for an in-depth discussion of the major theoretical issues and for a fresh confrontation of theory and experiment.

In addition to electrons, transport of other elementary excitations, such as e.g. spin excitations, excitons, and phonons are playing an increasingly important role in nanoscale devices. All the approaches mentioned above in the electron context can be applied to these excitations. Again an overarching theoretical issue is what level of first-principles theory is needed in all these contexts to achieve predictive value under realistic experimental conditions.

A related issue, for which only modest progress has been achieved so far, is how to deal with structural changes occurring in a device under transport conditions. In small conductive junctions the local current density can achieve very large values resulting in sizable forces acting on the atoms. How to couple finite bias conditions, electron transport and atomic dynamics beyond the harmonic approximation remains an open issue. An important problem in this context is that of current-induced ion transport or electromigration.

The quasi-particle (QP) band structure: All the above mentioned theories require the electronic ground state as a prerequisite. Recent developments of xc functionals towards a most reliable description of the ground state comprise the exact treatment of the exchange part (EXX), hybrid functionals, and approaches yielding a more accurate treatment of correlations (including van der Waals interactions). The question to which extent the *exact* solution of the Kohn-Sham equation would yield the proper QP band structure is one of the most fundamental issues in DFT. The choice of the functional, being the starting point of *GW* calculations, is also crucial for several open problems in MBPT as for example the issue of self-consistent *GW*.

The expected outcome of the program, comprising advances in several theoretical approaches, a better insight into physical processes at the atomic length scale, and consequently also at the meso- and macroscopic level, new developments of methods an in computer codes, and progress in the application of highly sophisticated theories to important questions in material science, will be a step towards computational materials design.

The suggested topics represent a breadth which easily justifies a 4.5 months program, e.g. we could start in the middle of November 2009 and close at the end of February 2010. The inclusion of February would be beneficial for participants from many universities who cannot attend the meeting during the semester due to their teaching load. Eliminating some topics from the program and focusing mainly on the

physics of excitation processes, would allow us also to run a shorter program of 2.5 - 3 months. However, we expect a much better outcome given the opportunity to discuss all the topics in detail.

Workshops and related activities:

We plan to have two workshops where in the first one with a duration of 5 days, the most recent achievements in electron-phonon coupling and nonadiabatic processes, will be discussed together with a survey of the most recent achievements in DFT, TDDFT and MBPT. The second one, somewhat shorter, will be dedicated to transport phenomena. In case of a 2.5 months program, we would prefer to have only one workshop of six days. Suggestions for invited speakers include B. Gadzuk, E. K. U. Gross, A. Knorr, R. Kosloff, S. Louie, J. Perdew, and J. Tully, who are among the key players in the field. Some of them have already told to stay at the program for an extended period of time (1-2 months), several others cannot commit themselves to stay for such a long time, but expressed their deep interest in attending the program for a period shorter than a month.

In addition, we will organize a hands-on workshop lasting for 10 days in order to teach modern computational methods to the young generation of scientists. Here Professor Spaldin from the ICMR expressed interest and offered partial support.

Besides the advancement of theoretical approaches and the computer-based training, code-development is another important issue. Being the basis for any application of advanced theories, it must aim to having reliable and most efficient tools in hand, which are applicable to any system up to the nano-scale. For this reason we will also invite and strongly encourage code developers to carry out long-term projects during the course of the program.

Coordinators:

The team of coordinators consist of Claudia Ambrosch-Draxl, Roberto Car, and Matthias Scheffler. C. Ambrosch-Draxl commits herself to stay for the whole duration of the KITP . She plans to be on sabbatical during this time. M. Scheffler has a part-time contract at UCSB, and spends usually 3 months per year in Santa Barbara. He will attend most of the program. R. Car commits himself to spending overall one month in Santa Barbara during the course of the program.

Key participants (those staying one month or longer)**:**

So far we have contacted several of the key players in the field. All of them immediately and enthusiastically agreed to participate and stay for more than a month. Among them are

Wilhelm Brenig (Germany)
Kieron Burke (USA)
Marilia Caldas (Brazil)
Rex Godby (GB)
Eberhard K. U. Gross (Germany)
Andreas Knorr (Germany)
Wei Ku (USA)
Börje Johansson (Sweden)
Andrew Rappe (USA)
Lucia Reining (France)
Warren E. Pickett (USA)
Angel Rubio (Spain)
John Tully (USA)
Troy Van Voorhis (USA)
Claudia Ambrosch-Draxl (Austria) organizer
Roberto Car (USA), organizer
Matthias Scheffler (Germany and USA), organizer

Other participants:

The interest in such program is very high, indeed. If necessary, we could immediately start contacting more people and send within a short period of time an even longer list of key players of this field who expressed interest to participate for at least 1-2 months. We also have an extended email list, including young researchers of the field, that would reach more than 1000 colleagues worldwide.

We will take care to put together a well-balanced community, as this will provide a most fruitful atmosphere.

Most of the participants will naturally come from the theory side, but we will also motivate (and have contacted already) experimentalists as well as people from industries to initiate a stronger interaction between theory, experiment, and the "real materials world". We expect at least 2-3 experimentalists per month, covering topics like semiconductor transport, femto-second spectroscopy, photo-emission experiments, catalysis or thermal barrier coating. We are confident that some of them will stay for 3-4 weeks, while representatives of industries (e.g. coming from IBM, Intel, Siemens Munich and Orlando, Pratt&Whitney, Osram, etc.) will typically come for a week only, most probably during the workshops going on.