Research Networking Programmes

Science Meeting – Scientific Report

Proposal Title: Electron-vibration coupling : theoretical and numerical challenges

1. Summary

The electron-vibration coupling has a ground-breaking importance in many fields of physics and chemistry and a huge impact on many elemental material properties. Despite this, most of its theoretical understanding builds upon model systems, while its first-principles derivation usually relies on a simple approach proposed 40 years ago. The present scientific meeting aimed at gathering the fragmented community of researchers working in this field fostering discussions and collaborations.

The workshop was held in the CECAM headquarters in Lausanne on May 27-29, 2015, and gathered more than 30 participants, including 14 speakers. It was structured in four sessions:

- Foundations and spectroscopy (3 presentations)
- Model Hamiltonians (2 presentations)
- Ab-initio approaches (6 presentations)
- Heat transport and thermoelectricity (3 presentations)

Most of the presentations were 30 minutes long, with 30 minutes discussion.
There were also three round tables to discuss future directions, each lasting one hour or more, as well as a poster session (May 27), and a social dinner (May 28).

Overall, we had excellent talks followed by very lively discussions. The format of the workshop fostered fruitful in-depth discussions that are usually prevented if most of the time is dedicated to presentations. Open questions that were brought up after the talks were further debated in the round-table meetings. The friendly atmosphere supported possible new collaborations to be established.

2. Description of the scientific content of and discussions at the event

State of the art

The electron-vibration (EV) coupling plays a key role in solids and nanostructures: renormalization of the electronic bands [1], transport in organic devices, governed by polarons [2,3,4], thermoelectricity [5], the position and intensity of Raman peaks [6,7], and different temperature-dependent or spectroscopic properties [8]. The EV coupling is also the driving force under the transition to superconducting state [9].

The EV interaction has been the subject of several fundamental studies thanks to such links with superconductivity and (polaronic) transport. However, its study in a coherent ab-initio framework beyond semi-empirical models, has received only very specific attention, mostly for the purpose of estimating the superconducting transition temperature. Indeed, the EV coupling strength has been computed from Density Functional Theory (DFT) for decades for that purpose. However, even in this context, the situation is not entirely satisfactory, see the recent result, based on GW, that Density-Functional Theory might strongly underestimate the EV coupling strength [10]. Most transport property calculations rely on (semi-)empirical estimations of electron scattering lengths by phonons, avoiding the explicit computation of EV coupling [5]. More generally, most ab-initio results (electronic or optical [11]) are obtained at zero Kelvin, while experiments directly include EV-effects, and also are performed at finite temperature. This is creating a gap between the ab-initio and experimental communities.

For spectroscopic purposes, the first works addressing the EV interaction, though relying on an atomistic description, appeared many years ago by Heine, Allen and Cardona (HAC) [1]. They pointed out that the EV coupling can induce corrections of the electronic levels as large as those induced by the electronic correlation. However their calculations were based on (1) semi-empirical methods and (2) static perturbation theory, neglecting dynamical effects. An slightly different route was pursued by Engelsberg and Schrieffer [12]. Surprisingly, it remained the state-of-the-art method for 40 years: many authors used it (or a simple extension of it) even in a first-principle context [13-16]. Recently, at last, dynamical effects have been addressed [17]. Concurrently, very recent experimental results have disclosed the complex dynamical structures that appear in the spectral functions of the prototypical TiO2 material [18]. A first-principles approach towards the understanding of such results is still lacking.

[1] See Allen, Cardona, Phys.Rev.B27, 4760 (1983), and refs therein
[2] Gosar, Choi, Phys.Rev.150, 529 (1966).
[3] Heeger, et al. Rev.Mod.Phys.60, 781 (1988)
[4] Vukmirovic, Bruder, Stojanovic, Phys.Rev.Lett. 109, 126407 (2012)
[5] See Xu, Verstraete, Phys.Rev.Lett.112, 196693 (2014), and refs therein
[6] Attaccalite, et al, NanoLetters 10, 1172 (2010).
[7] Gillet, Giantomassi, Gonze, Phys.Rev.B88, 094305 (2013)

[8] Noffsinger, et al, Phys.Rev.Lett. 108, 167402 (2012)
[9] Schrieffer, Theory of Superconductivity, Perseus Books, 1999
[10] See Antonius et al, Phys.Rev.Lett. 112, 215501 (2014) and refs therein.
[11] Onida, et al. Rev.Mod.Phys.74, 601 (2002)
[12] S. Engelsberg and J. R. Schrieffer, Phys. Rev. 131, 993 (1963).
[13] Eiguren, Ambrosch-Draxl, Phys.Rev.Lett.101, 036402 (2008)
[14] Capaz et al Phys.Rev.Lett.94, 036801 (2005)
[15] Marini, Phys.Rev.Lett.101, 106405 (2008)
[16] Giustino, et al. Phys.Rev.Lett.105, 265501 (2010)
[17] Cannuccia, Marini, Phys.Rev.Lett. 107, 255501 (2011)
[18] Moser et al, Phys.Rev.Lett.110, 196403 (2013)

Discussions at the workshop

As it is clear from the state-of-the-art section, despite the enormous interest in EV interaction and more and more scientists getting involved, this research field is still fragmented. There are many different methods and approaches to tackling different questions. This is inevitably creating a gap between the theoretical and experimental communities.

This workshop aimed at filling the gap that currently exists between the different above-mentioned communities.

In the following, we list several different topics, questions, and issues that were discussed. We also include details with which the speakers were feeding the discussion.

[TOPIC] Search of a systematic way to perform a perturbative treatment of the EV interaction in a pure ab-initio manner.
[DISCUSSION] This workshop was opened to theoreticians working both with ab-initio methods (Giustino, Gillet, Poncé, Montserrat, Côté, Shang, Calandra), like DFT, and with model Hamiltonians (Vukmirovic, Ortmann). Talks from both communities were scheduled for the first day. Those talks were followed by a round-table where the very different approaches were compared and discussed offering an unique opportunity for future developments.

[TOPIC] Is a perturbative treatment of the EV interaction suitable and accurate?
[DISCUSSION] The theories based on model Hamiltonians are not perturbative but they lack an atomistic description. The theories based, instead, on DFT have a solid atomistic basis but are perturbative. This workshop gave the opportunity to find concrete ways to merge the atomistic description with the non-perturbative treatment.

[ISSUE] What are the most relevant and recent achievements in the experimental community ?
[DISCUSSION] The session about spectroscopies had one talk given by a prominent experimentalist with a broad overview on the subject. The problems and perspectives opened by his presentation were discussed and confronted to the most recent theoretical and

numerical advances in the field. This offered a unique opportunity of assessing shortcomings and merits of both the theoretical and experimental point of view.

[ISSUE] One of the most used and widely spread assumption is that the EV interaction can yield only minor corrections (of the order of meV) to the electronic levels. As a consequence the majority of the simulations of the electronic and optical properties of a wide class of materials are generally performed by keeping the atoms frozen in their crystallographic positions.
[DISCUSSION] This workshop has shown theoretical and experimental proofs of the importance of EV interaction and that it needs to be included on all levels of electronic-structure theory. The in-depth discussions and the gathering of scientists belonging to very different research areas boosted such awareness.

[ISSUE] Phonons are harmonic excitations, and the harmonic approximation is known to be valid only for temperatures much lower than the Debye temperature. What happens above this temperature ? Are anharmonic corrections always negligible even at, for example, room temperature?
[DISCUSSION] There were several talks dedicated to anharmonic effects (Côte, Montserrat, Calandra), that represented an excellent source of discussions.

[ISSUE] Heat transport and thermoelectricity are intrinsically related to EV interaction. How can we quantitatively describe them?
[DISCUSSION] The specific section dedicated to heat transport and thermoelectricity represented, again, an excellent source of lively discussions and indicated the progress that has already been made during the last few years (Singh, Verstraete, Li).

3. Assessment of the results and impact of the event on the future directions of the field

This workshop aimed at starting to fill the gap between different communities and approaches, i.e. theory and experiment on the one hand, ab initio approaches and model hamiltonians on the other hand. Several key topics and ideas were intensively discussed, and other areas were identified where new land could still be explored.

Overall, we conclude from this that we have tackled very important questions. Obviously, it will need an appreciable amount of time time to (fully) answer them. However, this workshop has made significant progress to point to directions to go and thus advance the field.

The workshop has brought together people who will keep in contact to further advance different directions of research. Another outcome of this event is the plan to run similar workshops on a regular basis, including small discussion meetings and conferences of similar format as this event.

4. Program of the workshop

Day 1 - May, 27th 2015

- 08:30 to 09:00 - Registration
- 09:00 to 09:15 - Welcome and Introduction

Foundations and Spectroscopy

- 09:15 to 10:15 - **Feliciano Giustino**
  Quantum Nuclear Effects on the Electronic Structure of Molecules and Solids
- 10:15 to 11:15 - **Marco Grioni**
  High-energy spectroscopies: probing low-energy scales with high-energy photons
- 11:15 to 11:45 - Coffee Break
- 11:45 to 12:45 - **Yannick Gillet**
  First-principles study of frequency-dependent Resonant Raman scattering
- 12:45 to 14:00 - Lunch

Model Hamiltonians

- 14:00 to 15:00 - **Nenad Vukmirovic**
  Electron-phonon coupling constants for simulations of electronic transport in organic semiconductors
- 15:00 to 16:00 - **Frank Ortmann**
  Ab initio-Based Transport Approaches for Organic Semiconductors
- 16:00 to 16:30 - Coffee Break
- 16:30 to 18:00 - Round Table Discussion: Future Directions
- 18:00 to 20:00 - Poster Session

Day 2 - May, 28th 2015

Ab-Initio approaches

- 09:00 to 10:00 - **Samuel Poncé**
  Temperature Dependence of the Electronic Structure of Semiconductors and Insulators
- 10:00 to 11:00 - **Bartomeu Monserrat**
  Exploring the vibrational phase space: temperature dependence of band structures
- 11:00 to 11:30 - Coffee Break
- 11:30 to 12:30 - **Michel Côté**
  Dynamical and anharmonic effects on the electron-phonon coupling and the zero-point renormalization of the band structure
- 12:30 to 13:00 - **Honghui Shang**
  Electron-phonon Interaction Using Numeric Atom-centered Orbitals
- 13:00 to 14:00 - Lunch
- 14:00 to 15:00 - **Matteo Calandra**
  High-Pressure Hydrogen Sulfide from First Principles:A Strongly Anharmonic Phonon-Mediated Superconductor
- 15:00 to 16:00 - **Emmanouil Kioupakis**
  Phonon-mediated optical and Auger transitions in semiconductors
- 16:00 to 16:30 - Coffee Break
- 16:30 to 18:00 - Round Table Discussion: Future Directions

- 19:30 to 00:00 - Dinner

Day 3 - May, 29th 2015

Heat transport and thermoelectricity

- 09:00 to 10:00 - David Singh
  Complex Electronic Structures and Topological Insulators for Thermoelectric Materials
- 10:00 to 11:00 - Matthieu Verstraete
  Ab initio Seebeck coefficients
- 11:00 to 11:30 - Coffee Break
- 11:30 to 12:00 - Wu Li
  Ab-initio Electrical Transport Limited by Electron-Phonon Coupling from Boltzmann Transport Equation: Applications to Si, Al and MoS2
- 12:00 to 13:00 - Round Table Discussion: Future Directions
- 13:00 to 13:15 - Closing Word

5. List of participants (name + affiliation)

Organizers

Claudia DRAXL, Humboldt U. Berlin, Germany
Xavier GONZE, U.C. Louvain, Belgium
Andrea MARINI, National Research Council, Italy

Participants

Vladimir BACIC, Jacobs U. Bremene, Germany,
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