Report on CECAM workshop: Vibrational coupling: most important, often ignored, and a challenge for ab-initio theory

Lausanne, November 6 - 9, 2012

Sponsors: CECAM, Psi-k, MM1P.de

Organizers: Heiko Appel, Christian Carbogno, Claudia Draxl, Matthias Scheffler

Web page: `http://th.fhi-berlin.mpg.de/th/meetings/vc2012/`

1 Summary

We have organized and implemented a successful workshop on the ab-initio description of vibronic and vibrational couplings, held from November 6 - 9 at the CECAM headquarters in Lausanne. With the workshop we brought together researchers from different backgrounds but common interest in vibrational and vibronic couplings to identify and address open problems and challenges which are shared among the different fields. In each of these research areas there is a large body of specialized expertise available. We therefore were aiming to establish within the workshop a common forum to allow for an exchange of methodologies and to stimulate new developments which help to tackle the challenges posed by applications. The main goal of the workshop was to enhance the quality of theoretical and computational research on the various phenomena that are affected by electron-vibrational interactions.
The workshop was organized in a Gordon conference type format. Each topic was introduced by a discussion leader which also then moderated the invited talks of the corresponding session. Invited speakers lectured for 40 minutes, followed by 20 minutes of guided discussion. In total, the workshop encompassed 19 invited speakers and 20 poster contributions out of 42 participants and 4 organizers. Almost every participant was therefore actively contributing to the scientific discussions. We also reserved two evenings for poster sessions, which in particular gave younger participants a much broader stage to showcase their own research work. When we prepared the program of the workshop, we reserved ample time for discussion after the talks. This turned out to be essential to stimulate many discussions and often the critical points were only revealed in the discussion periods.

2 Description of the scientific content of and discussion at the event

Following the timeline of the workshop program, we briefly summarize below the main outcomes of the presentations given in the workshop.

The first day of the workshop was concerned with non-adiabatic effects that arise when the coupling of electrons and nuclei is treated beyond a standard ground-state Born-Oppenheimer description. After an introduction of H. Appel on experimental observables that are not properly captured in an adiabatic Born-Oppenheimer picture, E.K.U. Gross illustrated in his contribution how to make the Born-Oppenheimer approximation exact and thus gave a new perspective on potential energy surfaces and the non-adiabatic coupling of electrons and nuclei. In the second talk of the session, I. Tavernelli outlined how to compute non-adiabatic coupling matrix elements in first and second order response in a time-dependent DFT framework and exemplified the approach for protonated formaldimine and graphene. In the last talk of the first day, A. Horsfield illustrated the shortcomings of Ehrenfest dynamics and introduced the correlated electron-ion dynamics (CEID) approach, highlighting also the problems associated with the electron correlation in the CEID formalism. In the evening of the first day the first poster session took place. The session stimulated many lively discussions that extended way beyond the official end of the session.

The second day was devoted almost exclusively to thermoelectrics, an emerging hot topic in material science. A theoretical description of thermoelectric effects, i.e., the accurate assessment of (electronic) charge and (electronic and vibrational) heat transport at arbitrary low and high temperatures still constitutes a considerable challenge, as discussed and reviewed in the introductory talk by J. Sofo. On the same topic, but from quite a different perspective, J. Grin illustrated the challenges that experimentalist face in the search and engineering of novel and optimized themoelectric materials and how theory can aid and guide this process, for instance by disentangling the contributions that arise from changes in the character of the interatomic bonding. The following presentations discussed different techniques that have recently been developed and implemented in this context: B. Xu and N. Bonini critically examined how perturbational techniques based on state-of-the-art density functional theory allow to compute the transport coefficients at low temperatures and how these approaches can be extended to enable an assessment of the Seebeck coefficient and/or contributions arising from impurities, defects and alloying. Conversely, C. Carbogno and I. Savic focused on the higher (classical) temperature regime and discussed how molecular dynamics (MD) based approaches allow to tackle the problem of vibrational heat conduction. While C. Carbogno discussed the specific adaptions that MD techniques require when applied in first-principles frameworks, I. Savic presented the influence of meso- and nano-scopic structuring, as investigated by extended MD simulations on the basis of semi-empirical potentials. Last but not least, K. Reuter framed the previously discussed methodologies in a completely different light by presenting their potential application for problems in the field of heterogeneous catalysis and surface science.

The third day started with an introductory talk given by C. Draxl about the importance of electron-phonon coupling for accurate ab-initio electronic structure calculations, e.g., in the computation of band gaps at finite temperatures. In the following, F. Giustino discussed the perturbative treatment of the electron-phonon coupling and the role of various Feynman diagrams for different material classes (metal, insulators, superconductors). Along these lines, A. Eiguren illustrated the application of such concepts for the computation of quasi-particle spectra. Eventually, X. Gonze introduced the nuts & bolts of density functional perturbation theory, the underlying assumptions and the influence of the resulting Feynman diagrams (Fan

term, diagonal and non-diagonal Debye-Waller-term) on the band-gap of diamond. B. Batlogg opened the afternoon session of the third day by introducing the challenges that experimentalists face in the assessment, interpretation and description of vibrational and vibronic coupling in semiconductor materials and nanostructures. K. Hannewald then presented his theoretical approach to calculate mobilities in organic molecular crystals, going beyond narrow bands and small polarons. In the last talk of the day, M. Gl?ssl introduced a real-time path integral approach to describe the laser-driven carrier-phonon dynamics in semiconductor quantum dots. In the evening of the third day also the second poster session took place, which gave young participants again the opportunity to present their research work.

On the fourth and last day of the workshop the focus was then shifted to excitations in strong fields and time-resolved excitations. I. Franco opened the stage by addressing the role of vibronic couplings in non-equilibrium situations, decoherence and dephasing effects and related timescales. These aspects were then also taken up in the talk of O. Prezhdo who exemplified the role of dephasing, electron-phonon relaxation, and exciton formation in Silicon and PbSe quantum dots by means of of non-adiabatic molecular dynamics. E. Malic discussed in his talk the thermalization and cooling of graphene after optical excitation with a particular emphasis on orientational relaxation induced by phonons. In the last talk of the workshop R. van Leeuwen focused on the role of electron-phonon coupling in time-dependent quantum transport and non-equilibrium many-body theory and discussed the influence of vibronic effects on I-V curves, spectral functions and transient dynamics.

3 Assessment of the results and impact of the event on the future direction of the field

One recurring key point of the talks and of the discussions was the accuracy and correctness of density functional perturbation theory for the calculation of electron-phonon matrix elements. To date, there is no formal derivation or justification for this approach available in the literature. The presentations of C. Draxl, F. Giustino, A. Eiguren and X. Gonze impressively showed that a series of contributions beyond the current state-of-the-art perturbational treatment of the electronic structure are required to achieve a consistent description of vibrational-vibronic effects. Obviously, this fact calls for future collaborations and benchmarking of these approaches. Similarly, the presented electronic and vibrational transport calculations that are based on density functional perturbation theory might require revisitation under this light. As a matter or fact, this holds true for all transport methodologies presented on the third day of the workshop: Each of the discussed approaches (B. Xu, C. Carbogno, N. Bonini, I. Savic) has its own strengths and weaknesses; the underlying approximations limit the applicability of these techniques to certain fields, structures and thermodynamic regions. Naturally, a validation of the individual approaches requires a careful comparison of the different techniques with each other on the same footing, i.e., at the same level of electronic structure theory. Collaborations in this field can help establish a sound and unified theory of thermal and electronic transport, as required for further advancement in this area of research (Y. Grin). Another recurring aspect in the discussion sessions was the search for a reliable and scalable quantum-classical or quantum-

semiclassical method to study non-equilibrium dynamics beyond Ehrenfest. Current approaches fail e.g. to describe proper thermalization between electronic and nuclear degrees of freedom (Ehrenfest dynamics and related approaches), or are difficult to apply for metallic or small gap systems (surface hopping). Most prominent were also the repeated discussions on the expansion of Hamiltonians to higher order in the nuclear displacements, which introduces new vertices for Green's function approaches.

In summary, we think the workshop has been successful in identifing many open questions in the field of vibrational and vibronic coupling. As outlined above, the discussions revealed also several interesting directions for future research and developments which could help to tackle open problems. There were two main lines of research that emerged throughout the workshop: (i) vibronic pertubation theories centered around the Born-Oppenheimer approximation and (ii) non-adiabatic real-time dynamics of coupled electron-ion systems. We feel that it will be beneficial in future to pursue both directions in more detail. This should help researchers in the field to find tailored solutions for remaining open problems.

4 Program of the CECAM workshop: Vibrational coupling: most important, often ignored, and a challenge for ab-initio theory

Tuesday, November 6: Session I - Non-adiabaticity

14:40-15:00	Heiko Appel - Introduction to the session and discussion moderator
15:00-15:40	Eberhard K.U. Gross - How to make the Born-Oppenheimer approximation exact: A fresh look at potential energy surfaces and Berry phases in the time domain
15:40-16:00	Discussion
16:00-16:20	Coffee Break
16:20-17:00	Ivano Tavernelli - Nonadiabatic couplings and nonadiabatic dynamics within TDDFT
17:00-17:20	Discussion
17:20-18:00	Andrew Horsfield - How do you build a good Hamiltonian for CEID?
18:00-18:20	Discussion
18:20-19:30	Poster session

Wednesday, November 7: Session II - Thermoelectrics and heat transport

09:00-09:40	Jorge Sofo - Introduction to the session and discussion moderator
09:40-10:00	Discussion
10:00-10:40	Bin Xu - Ab initio thermoelectric properties
10:40-11:00	Discussion
11:00-11:20	Coffee Break
11:20-12:00	Christian Carbogno - Thermal Conductivity at High Temperatures from First Principles
12:00-12:20	Discussion
12:20-12:40	Peter Kratzer - Nanostructured semiconductors as thermoelectrics
12:40-14:00	Lunch Break

Wednesday, November 7: Session III - Thermoelectrics and catalysis

14:00-14:40	Juri Grin - Introduction to the session and discussion moderator
14:40-15:00	Discussion
15:00-15:40	Karsten Reuter - Watching phonons getting all excited during oxygen dissociation at Pd(100)
15:40-16:00	Discussion
16:00-16:20	Coffee Break
16:20-17:00	Nicola Bonini - Electrical and thermal transport from first-principles
17:00-17:20	Discussion
17:20-18:00	Ivana Savic - Towards realistic description of thermal transport processes in nanostructured materials
18:00-18:20	Discussion

Thursday, November 8: Session IV - Electronic excitations

09:00-09:20 Claudia Draxl - Introduction to the session and discussion moderator

09:20-10:00 Feliciano Giustino - Electron-phonon calculations across the board: from kinks to band gaps

10:00-10:20 Discussion

10:20-10:40 Coffee Break

10:40-11:20 Asier Eiguren - Self-consistent renormalization of quasi-particles; extending the range of applicability of the quasi-particle theory.

11:20-11:40 Discussion

11:40-12:20 Xavier Gonze - Temperature and zero-point motion effects on the electronic band structure

12:20-12:40 Discussion

12:40-14:00 Lunch Break

Thursday, November 8: Session V - Semiconductors and nanostructures

14:00-14:40 Bertram Batlogg - Introduction to the session and discussion moderator

14:40-15:00 Discussion

15:00-15:40 Karsten Hannewald - Polaronic signatures in the static and dynamical conductivities of organic crystals

15:40-16:00 Discussion

16:00-16:20 Coffee Break

16:20-17:00 Martin Gläßl - Real-time path integrals for laser driven carrier-phonon dynamics in quantum dots

17:00-17:20 Discussion

17:20-19:00 Poster Session

19:30-22:00 Social Dinner

Thursday, November 9: Session VI - Excitations in strong fields and time-resolved excitations

09:00-09:20 Ignacio Franco - Introduction to the session and discussion moderator

09:20-10:00 Oleg Prezhdo - Elastic and Inelastic Electron-Phonon Scattering in Nanoscale Materials

10:00-10:20 Discussion

10:20-10:40 Coffee Break

10:40-11:20 Ermin Malic - Ultrafast relaxation dynamics in graphene - Impact of carrier-phonon and carrier-carrier scattering

11:20-11:40 Discussion

11:40-12:20 Robert van Leeuwen - Electron-electron and electron-phonon interactions in time-dependent quantum transport using non-equilibrium many-body theory

12:20-12:40 Discussion

12:40 End of Workshop