Downfolding approach for charge-density-wave materials

Dynamics and thermodynamics in two-dimensional charge-density-wave systems

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In Short

- (Thermo-)Dynamics of charge density wave (CDW) systems can be obtained via computationally demanding molecular-dynamics (MD) simulations, which become prohibitive with increasing system size.
- Downfolding to effective low-energy models has proven to retain the accuracy of full first-principles calculations, while reducing computational requirements by several orders of magnitude, making MD simulations of large supercells feasible.
- Focus on open theoretical questions regarding CDW materials: phase transition into incommensurate CDW phase of 1H-$TaSe_2$ and dynamics of star of David CDW amplitude mode in 1T-TaS_2.

The coupling between electronic and nuclear degrees of freedom is an extremely complex problem of relevance to multiple branches of the natural sciences. In solids, this coupling plays an important role in the emergence of many-body instabilities, such as charge-density waves (CDWs). These periodic reconstructions are often, but not exclusively, found in the phase diagrams of low-dimensional materials. While the calculations of electronic and vibrational energies via so-called first-principles or *ab initio* methods using density-functional (perturbation) theory are still the state of the art, these simulations quickly become prohibitive with increasing supercell sizes needed to simulate real materials.

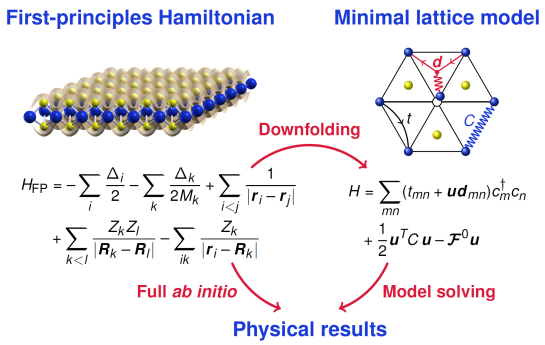

Figure 1: *Ab initio vs. ab initio based downfolding approaches to coupled electron-nuclear dynamics [1].*

To mitigate this problem, our group has developed a method to access the distorted states of a CDW material only based on the much more affordable *ab initio* calculations for the undistorted state [1]. This model is based on the concept of ***downfolding*** onto a minimal lattice model with linear electron-lattice coupling, where "minimal" refers to the dimension of the single-particle Hilbert space. For this, the electronic system is divided into so-called high- and low-energy sectors. The high-energy states are integrated out via field theoretical or perturbative means, leaving an effective low-energy model. The concept of this is depicted in Fig. 1. With this model, we are able to reproduce the strongly anharmonic free-energy landscape of various CDW materials and periodicities to a similar accuracy as full *ab initio* calculations via Quantum ESPRESSO [2]. Additionally, the calculations of the free energy and forces done with our downfolding code are about five orders of magnitude faster than comparable calculations via full *ab initio* methods [1], which allows us to study the thermodynamics of distorted phases on large supercells. This makes MD simulations of real materials feasible on long time scales in the order of multiple 100 ps.

To describe the thermodynamics of a CDW system, the PYTHON-based tight binding solver elphmod [3] was implemented in our group, which delivers the displacement field dependent forces and total free energies calculated via downfolding to the i-PI (path integral) MD engine used for the MD simulations [4]. The structure factor maps on the first Brillouin zone in Fig. 2 for replica-exchange and path-integral MD simulations (REMD, PIMD) are done for 1H-TaS_2 on an 18x18 supercell, simulated for 930 ps (REMD)/430 ps (PIMD) for four different temperatures. These supercell sizes and time scales are well beyond the computational capabilities of *ab initio* MD simulations, see the simulation of a 3x3 1H-NbS_2 CDW for time scales of about 6 to 12 ps in [5] using a similar amount of CPU hours. Therefore, this constitutes an extreme advantage of our downfolding code. At low temperatures, the clearly defined peak at crystal momentum $2/3\Gamma\mathrm{M}$ verifies the characteristic 3x3 CDW. For higher temperatures, it is broadened and reduced in intensity with the system transitioning into the symmetric phase. Transition temperatures follow with $T_{CL}\approx 96$ K and $T_{PI}\approx 82$ K. While the exact transition temperature for a 3x3 CDW in monolayer 1H-TaS_2 is not known, a comparable $T \approx 75$ K has been reported for bulk 2H-TaS_2 [6], showing the capability of our approach to describe

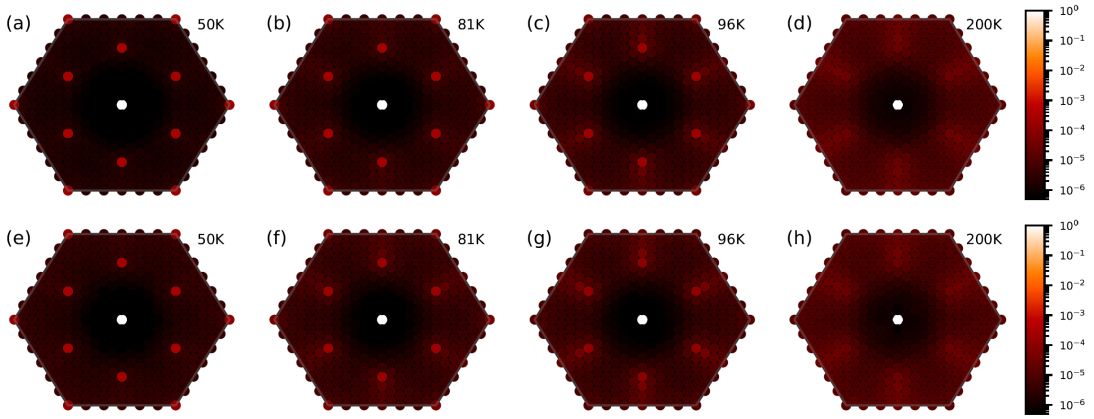

Figure 2: *Structure factors $\langle S(q)\rangle_T$ for the 3x3 CDW of 1H-TaS_2 on the 18x18 supercell. (a–d) S_{CL} calculated via classical MD simulations, (e–h) S_{PI} calculated via path integral MD simulations (PIMD). The bright peaks at q = 2/3 ΓM characterize the 3x3 CDW. At higher temperatures, the peaks are broadened and reduced in intensity with the system transitioning into the symmetric phase [1].*

transition temperatures in CDW materials.

During this project, we want to concentrate on two unresolved questions of particular interest for the dynamics and thermodynamics of two selected CDW materials:

1H-$TaSe_2$: We want to describe the phase transition between the commensurate and incommensurate phase in monolayer 1H-$TaSe_2$. At low temperatures, undoped 1H-$TaSe_2$ exhibits a 3x3 commensurate CDW. Upon heating, it undergoes a first-order transition into an incommensurate phase, followed by a second order transition at 122 K to the symmetric phase [7]. To describe the underlying thermodynamic effects, we want to compare classical MD simulations with path integral MD simulations incorporating quantum mechanical effects. Additionally, the doping of 1H-$TaSe_2$ shows a clear influence on the CDW phase transition temperatures [8], which we want to analyze in cooperation with the experimental group of Kai Rossnagel from the Christian-Albrechts university of Kiel.

1T-TaS_2: We will study the electron-lattice interaction and ultrafast dynamics of the star of David $\sqrt{13}$x$\sqrt{13}$ CDW amplitude mode. The coherent excitation of this mode has been measured experimentally in the oscillations of the spectral weight via femtosecond photoemission spectroscopy [9]. We plan to analyze the influence of the amplitude mode on the strength of the inter- and intralayer hopping for different dopings of monolayer and bilayer 1T-TaS_2 via band structure calculations. For this, we are collaborating with the experimental group of Uwe Bovensiepen from the university Duisburg-Essen.

WWW

https://for5249.org/index.html
https://www.physik.uni-hamburg.de/en/th1/ag-wehling.html

More Information

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Project Partners

K. Rossnagel (U Kiel), U. Bovensiepen (U Duisburg-Essen)

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