Ab initio downfolding: A thermometer for T_c and T_{CDW}?

Thermodynamics and superconductivity in two-dimensional charge-density-wave systems

***A. Schobert*[1], *J. Berges*[2], *N. Marzari*[2], *M. Rossi*[3], *and T. O. Wehling*[1,4]**, [1]*I. Institute of Theoretical Physics, University of Hamburg,* [2]*U Bremen Excellence Chair, Bremen Center for Computational Materials Science, and MAPEX Center for Materials and Processes, University of Bremen,* [3]*Max Planck Institute for the Structure and Dynamics of Matter, Center for Free, Electron Laser Science (CFEL), and* [4]*The Hamburg Centre for Ultrafast Imaging, University of Hamburg*

In Short

- Electronic-nuclear interactions in low-dimensional materials like transition metal dichalcogenides (TMDCs) give rise to phenomena such as charge-density waves (CDWs) and superconductivity, and research commonly uses fully *ab initio* techniques such as density-functional theory to understand their origin and competition.
- Our group developed a downfolding method that models the anharmonic free-energy landscape of distorted phases in TMDCs with similar accuracy as full *ab initio* calculations, but up to five orders of magnitude faster [cf. Fig. 1].
- This project aims to comprehensively study two-dimensional materials with a focus on the (thermo)dynamics of the CDW phase transition in the H-phase TMDCs [cf. Fig. 2] and the estimation of superconducting T_c in the presence of CDW distortions.
- Our research investigates the nature of the CDW phase transition in TMDCs, whether isoelectronic and isostructural compounds exhibit different CDW and superconducting physics, if downfolding can be used to speed up the standard *ab initio* workflow to calculate T_c, and if we can identify promising novel conventional superconductors.

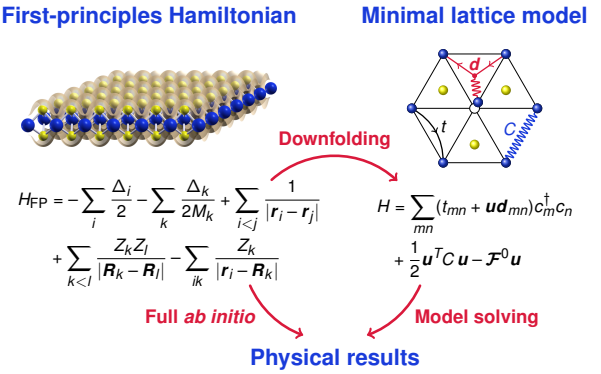

Figure 1: *Fully* ab initio *versus* ab initio *based downfolding approaches to coupled electron-nuclear dynamics. This scheme illustrates the complexity reduction from downfolding, which leads to computational speedups of several orders of magnitude.*

The interaction between electronic and nuclear degrees of freedom is a highly intricate problem that is relevant to various branches of natural sciences. In solids, this interaction plays a crucial role in the emergence of many-body instabilities, such as charge-density waves (CDWs) and superconductivity. These instabilities are frequently observed in the phase diagrams of low-dimensional materials, such as the two-dimensional transition metal dichalcogenides (TMDCs). Ongoing research aims to understand the emergence and competition between these phases, with theoretical investigations typically relying on first-principles or *ab initio* methods, such as density-functional theory (DFT) and its variants.

Isostructural and isoelectronic materials of the TMDC family, such as the trigonal-prismatic 1H-MX_2 (M = Nb, Ta; X = S, Se), exhibit similar behavior within DFT. On the harmonic level, the phonon dispersion predicts instabilities for the phonon wave vector q = 2/3 ΓM, which is commensurate with a 3 × 3 supercell. Structural optimization on the anharmonic free-energy surface for this supercell yields qualitatively similar distorted CDW ground states for all mentioned H-phase TMDCs. However, experimental observations reveal different CDW physics for these materials, with 2H-$NbSe_2$ (bulk) showing a measured CDW phase-transition temperature of T_{CDW} = 33 K, while no CDW order was observed in 2H-NbS_2 (bulk) [1,2]. The presence or absence of CDW has a significant impact on the observed superconductivity [3,4] in these materials at lower temperatures.

Previous theoretical studies have attempted to address the controversy between static DFT and experiment using state-of-the-art methods, such as *ab initio* MD [5] and the SSCHA [6]. While these methods have yielded useful insights, they are limited in their ability to provide a complete thermodynamic analysis across the CDW phase transition for the H-phase TMDCs. Additionally, calculations of superconducting critical temperatures T_c using Eliashberg theory, while still feasible on the 3 × 3 cell, are limited by coarse integration meshes and other factors [4].

To address these limitations, our group has developed a method [7] that relies on the so called *downfolding* approach [cf. Fig. 1]. It allows us to access

the distorted states based on *ab initio* calculations for the undistorted state. We have demonstrated that this method models the strongly anharmonic free-energy landscape of the H-phase TMDCs with similar accuracy as in full *ab initio* calculations. Furthermore, our method is five orders of magnitude faster in calculating free energy and forces, which allows us to study thermodynamics in the distorted phases on large supercells. This method also provides approximate phonon frequencies and electron-phonon coupling strengths for the distorted phase, which are crucial for calculating superconductivity.

The primary aim of this project is to conduct a thorough investigation of two-dimensional materials in distorted phases. Our first objective is to precisely simulate the (thermo)dynamics of the CDW phase-transition in the H-phase TMDCs [cf. Fig. 2], including properties such as heat capacity and phonon lifetimes. To date, there have only been two theoretical articles on this subject [5,6], one of which carried finite-size effects and the other which focused primarily on vibrational properties. We intend to offer insight into the thermodynamics of the CDW phase-transition using our new downfolding approach. By simulating large supercells, we aim to eliminate finite-size effects and approach the thermodynamic limit. Our second objective is to estimate superconducting T_c in the presence of CDW distortions at significantly reduced computational cost compared to the standard approach. We will validate our approach by comparing fully *ab initio* and downfolding-based critical temperatures for well-understood superconductors. Based on this, we will apply it to search for promising novel conventional superconductors.

In summary, we aim to answer the following scientific questions: Is the CDW phase-transition in TMDCs of first or second order? Will isoelectronic and isostructural compounds exhibit qualitatively different behaviour within the path-integral MD simulation? Can the standard *ab initio* workflow to calculate T_c be reliably speed up via downfolding? Can we identify promising novel conventional superconductors? Regardless of the outcome, we believe that answers to these questions will be of significant interest to the community.

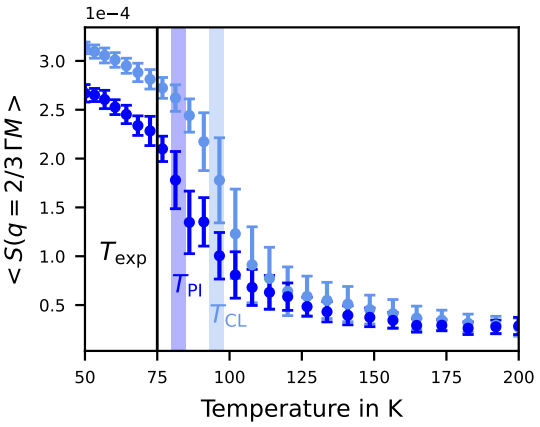

Figure 2: *Structure factor at the characteristic CDW wavevector q = 2/3 ΓM for the classical MD (light blue) and path-integral MD (blue). This quantity can be used to read off the phase-transition temperature T_{CDW}.*

WWW

https://www.physik.uni-hamburg.de/th1/ag-wehling.html

More Information

[1] I. Guillamón, H. Suderow, S. Vieira, L. Cario, P. Diener, and P. Rodière, *Phys. Rev. Lett.* **101**, 166407 (2008). doi:10.1103/PhysRevLett.101.166407

[2] M. Leroux, M. Le Tacon, M. Calandra, L. Cario, M-A. Méasson, P. Diener, E. Borrissenko, A. Bosak, and P. Rodière, *Phys. Rev. B* **86**, 155125 (2012). doi:10.1103/PhysRevB.86.155125

[3] C. Heil, S. Poncé, H. Lambert, M. Schlipf, E. R. Margine, and F. Giustino, *Phys. Rev. Lett.* **119**, 087003 (2017). doi:10.1103/PhysRevLett.119.087003

[4] C.-S. Lian, *Phys. Rev. B* **107**, 045431 (2023) doi:10.1103/PhysRevB.107.045431

[5] Y. Zheng, X. Jiang, X.-X. Xue, X. Yao, J. Zeng, K.-Q. Chen, E. Wang, and Y. Feng, *Nano Lett.* **22**, 1858 (2022) doi:10.1021/acs.nanolett.1c04015

[6] R. Bianco, I. Errea, L. Monacelli, M. Calandra, and F. Mauri, *Nano Lett.* **19**, 3098 (2019) doi:10.1021/acs.nanolett.9b00504

[7] A. Schobert, J. Berges, E. G. C. P. van Loon, M. A. Sentef, S. Brener, M. Rossi, and T. O. Wehling, *arXiv:2303.07261* (2023). doi:10.48550/arXiv.2303.07261

Funding

DFG via RTG 2247 (AS, TW) and EXC 2077 (JB)

DFG Subject Area

307-02