

O 53: Poster Session IV: Poster to Mini-Symposium: Frontiers of electronic-structure theory I

Time: Tuesday 13:30–15:30

Location: P

O 53.1 Tue 13:30 P

Broken adiabaticity induced by Lifshitz transition in MoS₂ and WS₂ single layers — ●DINO NOVKO — Institute of Physics, Zagreb, Croatia

The breakdown of the adiabatic Born-Oppenheimer approximation is striking dynamical phenomenon, however, it occurs only in a handful of layered materials. Here I show that adiabaticity breaks down in doped single-layer transition metal dichalcogenides in a quite intriguing manner. Namely, significant nonadiabatic coupling, which acts on frequencies of the Raman-active modes, is prompted by a Lifshitz transition due to depopulation and population of multiple valence and conduction valleys, respectively. The outset of the latter event is shown to be dictated by the interplay of highly non-local electron-electron interaction and spin-orbit coupling. In addition, intense electron-hole pair scatterings due to electron-phonon coupling are inducing phonon linewidth modifications as a function of doping. Comprehending these intricate dynamical effects turns out to be a key for mastering characterization of electron doping in two-dimensional nano-devices by means of Raman spectroscopy.

O 53.2 Tue 13:30 P

Ab initio study of Heat Capacities and Energy Dispersions in Antiferromagnetic L₁₀-type MnPt — ●KISUNG KANG, DAVID G. CAHILL, and ANDRÉ SCHLEIFE — Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

While antiferromagnetic L₁₀-type MnPt has been utilized as a pinning layer to apply exchange bias to a nearby ferromagnetic layer, the detailed physics of magnetism in MnPt is still under the veil. We investigate ground and excited states of antiferromagnetic L₁₀-type MnPt to understand their thermal and magnetic properties through the first-principles density functional theory. Ground-state calculations provide exchange coupling parameters, magnetocrystalline anisotropy, and metallic electronic band structure. Phonon and magnon dispersion curves are obtained from the finite difference method and linear spin-wave theory. At the Γ point a gap is expected in the magnon dispersion. Based on the energy dispersion results, we computed *ab initio* heat capacity for each elementary particle and the total heat capacity. The temperature dependence of the heat capacity at low temperatures originates mostly from phonons. There is almost no contribution from magnons because of the magnon gap and the low density of states in the low energy range. We use a Monte Carlo method based on the stochastic Landau-Lifshitz-Gilbert equation to compute the magnetic heat capacity in the high-temperature regime. Its peak provides the estimation of the Néel temperature, which shows good agreement with the measured value. *Illinois MRSEC NSF DMR-1720633

O 53.3 Tue 13:30 P

Surface Vibrations Enhance Intramolecular Hydrogen Tunneling in (some) Molecular Switches — ●YAIR LITMAN¹ and MARIANA ROSSI^{1,2} — ¹MPI for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany. — ²Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

Hydrogen atoms in supported molecular-switch architectures can tunnel close to room temperature, which calls for the inclusion of nuclear quantum effects (NQE) in the calculation of reaction rates even at high temperatures. However, standard approaches to introduce NQEs that rely on standard parametrized dimensionality-reduced models quickly become inadequate in these environments. Here, a paradigmatic molecular switch based on porphycene molecules adsorbed on metallic surfaces is addressed by full-dimensional calculations that combine density-functional theory for the electrons with the semiclassical ring-polymer instanton approximation for the nuclei[1]. Our results show that the double intramolecular hydrogen transfer (DHT) rate can be enhanced by orders of magnitude due to surface fluctuations in the deep tunneling regime. In addition, the origin of an Arrhenius temperature-dependence of the rate below the tunneling crossover temperature, as well as the transition to different regimes, is elucidated. With these considerations, a simple model is proposed to rationalize the temperature dependence of porphycene DHT rates spanning diverse fcc [110] surfaces. [1] Y. Litman, M. Rossi. Phys. Rev. Lett.

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O 53.4 Tue 13:30 P

The effects of quantum nuclei in metal-molecular interfaces — ●KAREN FIDANYAN^{1,2} and MARIANA ROSSI^{1,2} — ¹Fritz Haber Institute of the Max Planck Society, Berlin, Germany — ²Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

Hydrogen-containing molecular adsorbates on platinum-group metals often give rise to situations where the bond strength to the surface and its interplay with nuclear quantum effects (NQE) can substantially change the dynamics and equilibrium of hydrogen dissociation. In this work, we assess by means of density functional theory and path integral molecular dynamics simulations, interfaces involving non-polar molecules (cyclohexane) and polar molecules (water). For the cyclohexane/Rh(111) interface, we show that the H-Rh bond weakens the C-H bond and that NQE are responsible for a geometric isotope effect that is reflected on work-function changes. We further study the importance of simulating nuclear fluctuations including anharmonic effects, concluding that although these contributions play a pronounced role on these interfaces, most of them are concentrated on “classical” degrees of freedom, resulting in minor anharmonic quantum contributions in isotope effects [1]. For water on Pd(111) we investigate hydrogen dissociation under different potential voltage biases and analyze the impact of NQE within a quasi-harmonic approximation throughout the dissociation path.

[1] K. Fidanyan, I. Hamada and M. Rossi, arXiv:2010.03970 (2020)

O 53.5 Tue 13:30 P

Tunnelling with Non-Adiabatic Effects: H-Diffusion in Pd — ●ESZTER SAROLTA PÓCS¹, YAIR LITMAN¹, and MARIANA ROSSI^{1,2} — ¹MPI for the Structure and Dynamics of Matter, Hamburg, Germany — ²Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Hydrogen diffusion in metals is a fundamental process in areas like energy storage devices and hydrogen separation membranes. However, the accurate theoretical description of it is challenging because (1) nuclear quantum effects (NQEs) such as nuclear tunnelling play an important role even at room temperature due to the light mass of the hydrogen atom; (2) the excitation and relaxation of electron-hole pairs around the Fermi level give rise to non-adiabatic effects (NAEs) that alter the system dynamics. In this work, we present a novel approach that combines the ring polymer instanton formalism [1] with *ab initio* electronic friction [2,3], allowing us to include both NQEs and NAEs in the rate-calculation of H-diffusion between interstitial sites of Pd. Our approach has been implemented into the i-PI code [4] including the spatial dependence of the electronic friction tensor which facilitates the study of nuclear tunnelling on metallic systems with unprecedented realistic first-principles simulations.

[1] J. O. Richardson, *JCP* **144**, 114106 (2016). [2] M. Head-Gordon, J. C. Tully, *JCP* **96**, 3939 (1992). [3] R. J. Maurer, M. Askerka, V. S. Batista, J. C. Tully, *PRB* **94**, 115432 (2016). [4] V. Kapil, *et al.*, *CPC* **236**, 214 (2019).

O 53.6 Tue 13:30 P

Nonadiabatic renormalization of electron-phonon interaction in graphene-based materials — ●NINA GIROTTO and DINO NOVKO — Institute of Physics, Zagreb, Croatia

Some of the most prominent features of two-dimensional (2D) materials issue from electron-phonon coupling (EPC) and are easily tailored by strain and doping. Phonon-mediated superconductivity is expected in a variety of 2D materials, and because the transition temperature within the Bardeen-Cooper-Schrieffer (BCS) theory increases with increasing EPC, tailoring EPC provides a recipe for a more feasible realization of superconductors. Here, we present density-functional-theory (DFT) calculations of EPC properties of doped 2D systems, specifically highly-doped graphene and hole-doped graphane. Doping equalizes the energy scales of electron transitions and phonon frequencies, but using the adiabatic Born-Oppenheimer approximation, DFT assumes nuclear and electronic motion can be separated. We show that the mentioned approximation is not applicable on studied systems, since the adiabatically obtained phonon spectrum is at significant variance with the one containing nonadiabatic corrections. Nonadiabatic

renormalization greatly modifies the EPC strength, which in turn alters the superconducting transition temperature prediction, rendering its calculation more reliable. The importance of including dynamical corrections is indisputable and care should be taken when neglecting nonadiabatic effects as they have a huge impact not only on the magnitude of the EPC strength and the transition temperature, but also on the qualitative understanding of the system in question.

O 53.7 Tue 13:30 P

Polaron and multi-charged states in extended p-conjugated systems: the role of electron correlation. — •DANIELE FAZZI¹, KLAUS MEERHOLZ¹, and FABRIZIA NEGRI² — ¹Institut für Physikalische Chemie, Department Chemie, Universität zu Köln, Greinstr. 4-6, D - 50939 Köln — ²Dipartimento di Chimica, Università di Bologna, via F. Selmi, 2, 40126 Bologna, Italy

Polarons play a crucial role in governing charge and energy transfer in organic functional materials. An accurate description of their elec-

tronic structure and electron-phonon couplings is mandatory to assess their response and transport properties.

We report a comprehensive investigation of polarons in ladder-type conjugated polymers [1-3]. Polarons show a polyradicaloid character, as revealed by combining broken-symmetry density functional theory, fragment orbital density analysis, and multireference methods [3]. Electron and hole polarons relaxed on localised states, however showing different structural and electron-phonon coupling properties. Polarons, bipolarons and multi-charged states reveal a complex scenario of quasi-degenerate states, each featuring various spin multiplicity and response properties.

Our study provides insights towards the understanding of doping processes and insulator-to-conductor transitions in ladder-type polymers considered for energy-saving applications.

[1] Wang, S., et al., *Adv. Mater.* 2018, 30, 1801898. [2] Fazzi D., et al., *J. Mat. Chem. C.*, 2019, 7, 12876-12885. [3] Fazzi D., et al., *Adv. Electron. Materials*, 2020, 2000786.