VISTA

VISTA Seminar

Seminar 31

February 16, 2021

10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT / 4:00 pm – 5:30 pm Paris

TOC:
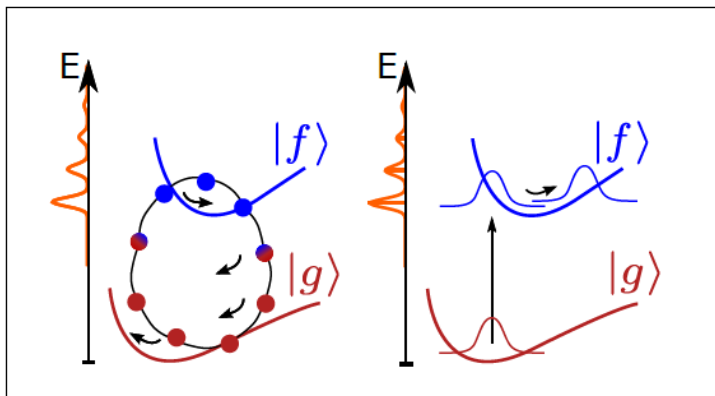
Vibronic Spectroscopy with Classical Trajectories

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Vibronic spectra provide a fingerprint of the coupling between electronic and nuclear degrees of freedom and thus between electronic structure and molecular geometry. Well resolved vibronic spectra of small to medium-sized molecules can be obtained, e.g., for gas phase or liquid helium droplet conditions. The standard analysis assumes shifted harmonic potentials leading to a superposition of Franck-Condon progressions with the electron-vibrational coupling being quantified by the Huang-Rhys factors of the different vibrational modes. Performing accurate quantum dynamical simulations including effects, e.g., due to Dushinsky rotation, anharmonicity, and nonadiabatic transitions, is a demanding task, if not impossible for larger molecules. Therefore, it is tempting to resort to classical trajectory-based approaches having a more favorable scaling with system size. Surprisingly, it turns out that reproducing a well-resolved vibronic progression provides a serious challenge for trajectory-based methods even at the level of a single vibrational coordinate.

The link between molecular dynamics trajectories and vibronic spectra is provided by time correlation functions of the energy gap between the considered electronic states [1,2]. To incorporate quantum effects in the sampling of the nuclear distribution the imaginary-time path integral approach can be used [3]. At this point one normally has to decide on which state the distribution of nuclear coordinates is sampled. Unfortunately, common choices such as ground or excited state or the averaged classical limit yield rather different results, none of them being very accurate. Therefore, a modified correlation function has been proposed, which is capable of incorporating information on the potential energy surfaces of both involved states simultaneously [3]. This leads to a considerable improvement, but not yet perfect agreement. Alternatively, a modification of the so-called Matsubara ansatz has been suggested and shown to yield an almost quantitative agreement with exact quantum dynamics results at least for the one-dimensional test cases considered [4].

[1] S. Karsten, S. D. Ivanov, S. G. Aziz, S. I. Bokarev, O. Kühn, J. Phys. Chem. Lett. **8**, 992 (2017)
[2] S. Karsten, S. D. Ivanov, S. G. Aziz, S. I. Bokarev, O. Kühn, J. Chem. Phys. **146**, 224203 (2017)
[3] S. Karsten, S. D. Ivanov, S. I. Bokarev, O. Kühn, J. Chem. Phys. **148**, 102337 (2018)
[4] S. Karsten, S. D. Ivanov, S. I. Bokarev, O. Kühn, J. Chem. Phys. **149**, 194103 (2018)

Real-time TD-DFTB simulations and modeling of Fano-induced transparency in molecular van der Waals Heterostructures

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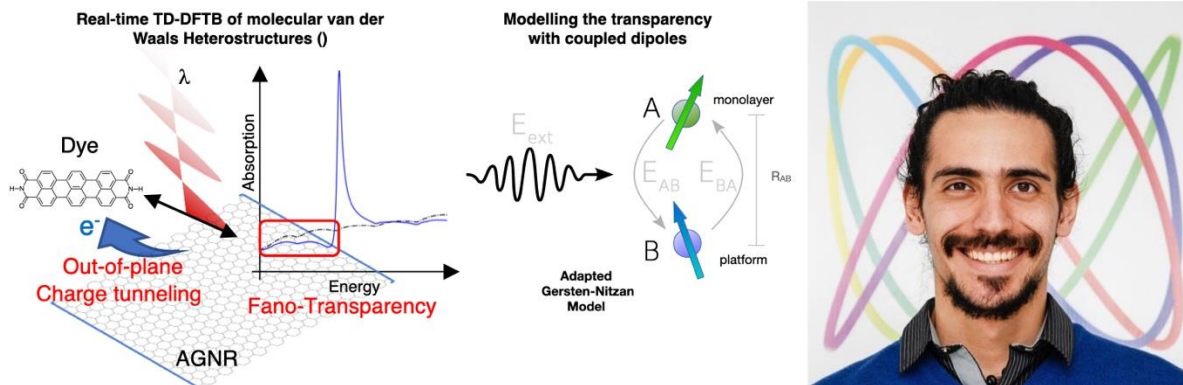
Complex van der Waals heterostructures from layered molecular stacks are promising optoelectronic materials offering means to efficient, modular charge separation and collection layers. While gating and doping in two-dimensional (2D) materials is well-known [1-3], the physics of photosensitizing and advanced optical properties have not been fully investigated, especially in the context of molecular vdW heterostructures (MVHs), that is, regular monolayer stacks on 2D materials [3]. The effect of stacking in the electrodynamics of such hybrid organic–inorganic two-dimensional materials remains largely unexplored, whereby molecular scale engineering could lead to advanced optical phenomena. For instance, tunable Fano engineering could make possible on-demand transparent conducting layers or photoactive elements, and passive cooling. In a recent work [4], we employed an adapted Gersten-Nitzan [5] model and real time time-dependent density functional tight-binding [6] to study the optoelectronics of self-assembled monolayers on graphene nanoribbons. We found Fano resonances [7] that cause electromagnetic induced opacity and transparency and reveal an additional incoherent process leading to interlayer exciton formation with a characteristic charge transfer rate [4]. These results showcase hybrid van der Waals heterostructures as paradigmatic 2D optoelectronic stacks, featuring tunable Fano optics and unconventional charge transfer channels. Our findings open a path for improved design of modular multilayer organic photovoltaic devices.

References

[1] Gobbi, M., et al. When 2D Materials Meet Molecules: Opportunities and Challenges of Hybrid Organic/Inorganic van der Waals Heterostructures. Advanced Materials, 30(18), 1–20 (**2018**).

[2] Wehling, T. O., et al. Molecular doping of graphene. Nano Letters, 8(1), 173–177 (**2008**).

[3] Wieghold, S., et al. Photoresponse of supramolecular self-assembled networks on graphene-diamond interfaces. *Nature Communications*, 7, 1–8 (**2016**).

[4] Lien-Medrano, C. R., et al. Fano Resonance and Incoherent Interlayer Excitons in Molecular van der Waals Heterostructures. *Nano Letters*, (**2022**).

[5] Gersten, J., & Nitzan, A. Electromagnetic theory of enhanced Raman scattering by molecules adsorbed on rough surfaces. *The Journal of Chemical Physics*, 73(7), 3023–3027 (**1980**).

[6] Bonafé, F. P., et al. A Real-Time Time-Dependent Density Functional Tight-Binding Implementation for Semiclassical Excited State Electron–Nuclear Dynamics and Pump–Probe Spectroscopy Simulations. *Journal of Chemical Theory and Computation*, 16(7), 4454–4469 (**2020**).

[7] Limonov, M. F., et al. Fano resonances in photonics. *Nature Photonics*, 11(9), 543–554 (**2017**).

How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 31
Time: Feb 16, 2022 10:00 AM Eastern Time (US and Canada)

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