Theoretical and Physical Chemistry Institute

National Hellenic Research Foundation

Vass. Constantinou 48, Athens

LECTURE

"First-principles modeling of excited states of molecules and solids at finite temperatures: phonon-induced localization, dissociation and screening"

Dr. Antonios M. Alvertis

Research Scientist,

NASA Ames Research Center,

Affiliate at Lawrence Berkeley National Lab,

Berkeley, USA

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First-principles modeling of excited states of molecules and solids at finite temperatures: phonon-induced localization, dissociation and screening

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The excited state properties of semiconducting and insulating solids are critical to numerous applications, including optoelectronics devices such as photovoltaics and LEDs. These devices typically operate at room temperature; however, most theoretical first-principles approaches ignore finite-temperature effects on excited states. This is due to significant challenges associated with including finite temperature effects into the vast majority of theoretical methods that describe the excited states of solid-state systems. As a result, there is currently a significant disconnect between theory, experiment, and practical applications in this field.

In this talk I will present a theoretical framework within many-body perturbation theory to account for finite temperature effects on the excited states of any crystalline and molecular solid, extending the widely used *ab initio* GW-Bethe Salpeter Equation (BSE) approach.

In the first part of the talk, I will demonstrate how finite displacement methods can be used alongside GW-BSE, to understand the temperature-dependent excited state (exciton) bandwidth of molecular crystals due to phonon-induced exciton localization [1], including the important role of anharmonic phonons [2], and revealing pathways towards efficient energy transfer. High-frequency phonons are found to couple weakly to delocalized excitations [3], allowing us to demonstrate design rules for minimizing non-radiative recombination losses in organic systems, demonstrating some of the world's most efficient LEDs [4]. In the second part of the talk, building on a framework introduced in prior work [5], I will present a first-principles extension of GW-BSE to include phonon screening of excited states at finite temperatures. Using an efficient computational implementation of this scheme [6], we demonstrate strong temperature dependence of exciton binding energies in several systems, as well as accurate predictions of exciton dissociation rates towards free charge carriers [7].

[1] Alvertis, Haber, Engel, Sharifzadeh, Neaton, Phys. Rev. Lett. **130**, 086401, (2023)
[2] Alvertis, Engel, Phys. Rev. B **105**, L180301, (2022)
[3] Alvertis *et al*. Phys. Rev. B **102**, 081122(R), (2020)
[4] Ghosh, Alvertis *et al*. submitted (2023)
[5] Filip, Haber, Neaton, Phys. Rev. Lett. **127**, 067401 (2021)
[6] Li, Alvertis, Gant, Neaton, Louie, in preparation
[7] Alvertis, Haber, Li, Coveney, Louie, Filip, Neaton, submitted (2023)