Capturing tunnelling, wavepacket splitting and single vibronic level excitation effects on vibronic spectra with Hagedorn wavepackets

Z. Zhang[1], J. Vaníček[1]*

[1]Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne

Vibrationally resolved electronic spectroscopy provides important information on the structure and dynamics of polyatomic molecules. On-the-fly ab initio implementation [1,2,3] of the thawed Gaussian approximation (TGA) [4] has been successful in describing such spectra within the Condon approximation but cannot capture non-Condon effects, tunneling or wavepacket splitting. While the extended TGA [5,6] captures first-order non-Condon effects, Hagedorn's wavepackets [7,8], i.e. superposition of states, each of which is the Gaussian multiplied by a cleverly chosen polynomial, enable the propagation of non-Condon wavepackets of arbitrary shapes. I will demonstrate that a variational implementation [9] of the Hagedorn wavepackets can capture tunneling and wavepacket splitting, as well as their effects on spectra. To demonstrate that the method is not restricted to small model systems, I will combine our recently developed algorithm for an algebraic evaluation of the overlap of Hagedorn wavepackets with on-the-fly ab initio semiclassical dynamics to compute single vibronic level fluorescence spectra of polyatomic molecules.

[1] M. Wehrle, M. Šulc, J. Vaníček, J. Chem. Phys., **140**, 244114 (2014)
[2] M. Wehrle, S. Oberli, J. Vaníček, J. Phys. Chem. A, **119**, 5685-5690 (2015)
[3] T. Begušić, E. Tapavicza, J. Vaníček, J. Chem. Theory Comput., **18**, 3065-3074 (2022)
[4] E. Heller, J. Chem. Phys, **62**, 1544-1555 (1975)
[5] A. Patoz, T. Begušić, J. Vaníček, J. Phys. Chem. Lett., **9**, 2367-2372 (2018)
[6] A. Prlj, T. Begušić, Z. Zhang, G. Fish, M. Wehrle, T. Zimmermann, S. Choi, J. Roulet, J. Moser, J. Vaníček, J. Chem. Theory Comput., **16**, 2617-2626 (2020)
[7] G. Hagedorn, Annals of Physics, **269**, 77-104 (1998)
[8] C. Lasser, C. Lubich, Acta Numerica, **29**, 229-401 (2020)
[9] E. Faou, V. Gradinaru, C. Lubich, SIAM J. Sci. Comput., **31**, 3027-3041 (2009)