

# Electronic-vibrational coupling in a self-contained density functional framework

Ryan Requist<sup>1</sup>, C. R. Proetto<sup>2</sup>, E. K. U. Gross<sup>1</sup>

<sup>1</sup>*Fritz Haber Center for Molecular Dynamics, Hebrew University of Jerusalem, Israel*

<sup>2</sup>*Centro Atómico Bariloche and Instituto Balseiro, Argentina*

Density functional theory predicts the electronic structure of molecules and solids constrained to their ground state adiabatic potential energy surfaces. While this picture is usually accurate near the equilibrium structure, it can break down near conical intersections and during chemical reactions and charge transfer processes due to coupling to other Born-Oppenheimer eigenstates. We focus on the nonadiabatic effects of electronic-vibrational coupling and show that they can be efficiently incorporated in a seamless density functional framework [Phys. Rev. B 99, 165136 (2019)]. The Kohn-Sham potential acquires a dependence on the wave function of the nuclei [J. Chem. Phys. 148, 084110 (2018)], in distinction to conventional DFT. The nuclear wave function in turn obeys the Schrödinger equation derived in the exact factorization method [Phil. Trans. Roy. Soc. A 372, 20130059 (2014)]. Nonadiabatic phonons are defined as the harmonic vibrations of this equation, which may contain a nontrivial vector potential. A simple orbitaldependent functional approximation reproduces the leading-order nonadiabatic effects, e.g. electronic band structure renormalization, in the Fröhlich model.