Computing Molecular Excited States and Spectra with Neural-Network-Supported Configuration Interaction

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Our newly developed Python library for selective configuration interaction (CI) calculations of fermionic quantum systems, SOLAX [1], is applied to compute the ground and excited electronic states of molecules. We employ a novel state-specific CI approach, where the Hartree-Fock reference is obtained by variationally optimizing the orbitals for a specific excited state in a plane-wave representation [3]. Both full CI and selective CI calculations are performed, the latter using a recently proposed Neural-Network Supported CI approach (NNCI) [2]. The performance of the method is assessed by analysing the expansion of the many-body states in the Slater determinant basis and the distribution of relevant configurations. Preliminary calculations on Rydberg excited states of the H_2, N_2, and NH_3 molecules indicate that variationally optimizing the orbitals for the excited state not only improves mean-field solutions [3] but also improves the efficiency of the CI calculations, as accurate results are achieved with fewer relevant determinants compared to calculations using ground state optimized orbitals. Additionally, we present a newly implemented SOLAX algorithm to compute spectral functions within the NNCI scheme without the need for an explicit calculation of excited eigenstates and show how our methodology bridges the interdisciplinary gap between quantum chemistry and theoretical solid state physics.

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[2] Yorick L. A. Schmerwitz, Louis Thirion, Gianluca Levi, Elvar Ö. Jónsson, Pavlo Bilous, Hannes Jónsson, and Philipp Hansmann, "A Neural-Network-Based Selective Configuration Interaction Approach to Molecular Electronic Structure," *Journal of Chemical Theory and Computation* (2025)

[3] Alec E. Sigurdarson, Yorick L. A. Schmerwitz, Dagrún K. V. Tveiten, Gianluca Levi, and Hannes Jónsson, "Orbital-optimized density functional calculations of molecular Rydberg excited states with real space grid representation and self-interaction correction," *The Journal of Chemical Physics* (2023)