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Topological Photophysics in Molecular Aggregates: The Role of Charge-Transfer States

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Topological band theory links global properties of periodic wave functions to robust boundary and interface phenomena. Transferring this concept to molecular excitonic materials is appealing because molecular packing controls excitonic couplings and could therefore provide a chemical route to localizing and directing optical excitations. Real molecular aggregates, however, are not simple Frenkel-exciton lattices: nearby charge-transfer (CT) configurations can modify the excitonic band structure and generate localized states that resemble topological edge modes. We investigate this interplay in perylene-bisimide aggregates using symbolic configuration interaction (SymbolicCI), a fragment-based approach that constructs ab initio aggregate Hamiltonians in a chemically interpretable basis of Frenkel and CT configurations [1,2]. These atomistic Hamiltonians are used to test periodic hybrid Frenkel–CT lattice models. Exact Feshbach elimination shows that the reduced Frenkel problem is generally energy dependent rather than a static Su–Schrieffer–Heeger Hamiltonian. Candidate topological phases are therefore evaluated using isolated gaps and inversion indicators of the explicit multiband spectrum, adiabatic continuity to the controlled SSH limit, and separate finite-chain boundary diagnostics. We find that a broad range of apparent SSH inversions predicted by static downfolding collapses to a narrower set of inversion-nontrivial multiband gaps when the CT sector is restored. Charge transfer plays a dual role: differential CT dressing can reverse the effective dimerization in the idealized model, but CT-rich boundary states can also imitate topological localization. In the microscopic PBI candidate, destructive interference suppresses the nearest-neighbour splitting to the resolution limit of the mapping, where longer-range couplings invalidate a two-bond SSH description. The resulting states differ in excitonic character, localization, oscillator strength, and expected field response. These results define the conditions under which SSH-like topology can be meaningfully assigned in molecular excitonic materials.

[1] A. Singh and M. I. S. Röhr, J. Chem. Theory Comput. 20, 8624–8633 (2024).
[2] J. E. Adelsperger, C. de Graaf, and M. I. S. Röhr, J. Chem. Theory Comput. 22, 4201–4217 (2026).