

First-Principles Exciton Models

John M. Herbert*, Adrian F. Morrison, and Jie Liu†

Dept. of Chemistry & Biochemistry, The Ohio State University, Columbus, OH 43210

We describe an efficient and highly-parallelizable algorithm for investigating collective excitations in molecular crystals and aggregates, based on an *ab initio* implementation of a Frenkel-Davydov exciton model. Collective excitations are described in a basis composed of direct products of monomer excitations, and coupling matrix elements are computed without the need for the sorts of approximations (nearest-neighbor, neglect of exchange, dipole-coupling, etc.) that are often used in more traditional exciton models. Calculation of both the monomer basis states and the couplings is readily distributable across processors, and accuracy of ~ 0.1 – 0.2 eV with respect to supersystem calculations is achievable, with a model that is applicable to the equivalent of $\approx 55,000$ basis functions on 450 processors in < 1 week of wall time. Preliminary applications have been made to singlet fission in crystalline tetracene and to excitonic energy transfer in a self-assembling organic semiconductor nanotube.

We have also shown how time-dependent density functional theory (TDDFT) calculations in similar systems can be accelerated by the application of excitonic approximations to the underlying equations, by eliminating transition amplitudes that connect different monomer units but computing excitonic couplings between localized excited states. This approach can successfully describe *delocalized* excitations, as in the aforementioned semiconductor nanotube, again with an accuracy of $\lesssim 0.2$ eV with respect to the full TDDFT calculation. A particular promising application of this approach, however, is to study *localized* excitations in supermolecular systems, *e.g.*, to include explicit solvent molecules in a TDDFT calculation of a solution-phase chromophore. By use of distributed computing, additional solvent molecules can be included at negligible wall-time cost and with negligible loss of accuracy with respect to a supersystem TDDFT calculation, and in a way that eliminates spurious charge-transfer-to-solvent excitations. Using this approach, solution-phase TDDFT calculations can readily be converged with respect to the number of solvent molecules that is described quantum-mechanically.

*herbert@chemistry.ohio-state.edu

†Present address: Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany