Excitations in Large Systems using Transition-Based Constrained Density Functional Theory

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The ability to accurately predict excited state energies is crucial for investigating molecules and materials, both from a fundamental and applied perspective. For example, thermally activated delayed fluorescence (TADF) has recently proven to be a promising mechanism, which can be exploited for efficient and environmentally friendly organic LEDs. One of the key parameters required for TADF is a small singlet-triplet splitting, making it an important property for investigating and designing new emitters. However, this is complicated by the fact that such excitations may be a combination of both local and charge transfer character, while also being influenced by both internal disorder and the surrounding environment, posing a significant challenge for existing excited state methods. This has motivated the development of a new method, named transition-based constrained DFT (T-CDFT), wherein a constraint is imposed between orbitals, rather than a region of space. This allows the treatment of both local excitations and charge transfer states at a computational cost similar to ground state calculations. T-CDFT has been implemented in the linear-scaling BigDFT code, thereby providing a framework for including explicit environmental and statistical effects on excited state calculations of disordered supramolecular materials, including those used in TADF-based OLEDs.