

ARE CLUSTER APPROACHES USEFUL FOR DESCRIBING THIN FILMS OF ORGANIC SEMICONDUCTORS?

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ABSTRACT

Organic semiconductors have been intensively studied for decades. However, shortcomings in the theoretical description of the photo physics of the thin films of organic semiconductors still prevent a precise understanding of the complex interplay of the various processes that determine the photophysical properties of these thin films. So far, cluster approaches which have been able to explain many very different photophysical phenomena appearing in various organic semiconductors,¹ have failed to reproduce the absorption spectra of thin films of pentacene. The computed absorption bands are too high, and the energetic sequence of the bands cannot be reproduced. Reasons for these shortcomings remained unclear.² In contrast, G_0W_0 /BSE calculations³ using periodic boundary conditions achieve semi-quantitative agreement. However, these approaches differ from highly correlated wave function-based methods for dimers. So, the question of error compensation effects arises.

In the present work we describe our recent approach. It combines cluster approaches with optimal-tuned functionals. In a first step we investigate the pentacene monomer to benchmark various DFT approaches. The system is sufficiently small for high-level wave-function-based approaches and unambiguous experimental results are available. In the second step we show that our approach achieves very accurate results (errors < 0.1 eV) if some rules are obeyed. We discuss the rules and the underlying reasoning using pentacene, tetracene and perfluoropentacene as examples.

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