EXCITONIC COUPLED-CLUSTER THEORY FOR LARGE-SCALE ELECTRONIC STRUCTURE CALCULATIONS: TEST APPLICATION AND OUTLOOK

Starting a few decades ago, enormous progress has been made in performing useful chemical simulations by decomposing large systems into fragments. Notwithstanding this progress, a more favorable ratio of accuracy to computational cost is always desirable to broaden the coverage of reliable simulations, especially if the phenomenon under investigation hinges on small energy differences or involves a complex electronic structure.

One shortcoming of presently available fragment-based methods is that electron correlation (if included) is modeled at the level of individual electrons. We have shown that a super-system Hamiltonian may rigorously be rewritten in terms of sub-system fluctuations (the exciton basis), to which traditional electronic structure methods, such as coupled-cluster theory, can be applied. This nascent concept has only recently been extended to real electronic systems, allowing also for inter-fragment electron exchange and charge transfer. Tests on chains of up to 100 Be atoms show dramatic increases in efficiency over traditional methods of comparable accuracy.

Although still in its infancy, the true power of this method lies in the straightforward way that accuracy can be carefully controlled and manipulated in a spatially inhomogeneous way. Difficult electronic structure problems may be embedded in complex environments, and the extension to excited states is straightforward, opening the door to time-dependent studies of condensed-phase energy and charge transfer. Some target applications will be outlined.

Refreshments served at 1:45 pm in 331 Klamath Hall

Hosted by Jeff Cina