Efficient Electronic Structure Approaches for Organic & Nano Materials

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We present a hierarchy of hybrid approaches for embedded many-body expansions combined with local approximations to enable expedited first principles calculations of organic materials properties. We demonstrate calculations of deformation in response to external electric and mechanical stimuli within this framework, as is required to assess applications as responsive materials (e.g. piezoelectric sensors, shape-shifting electromechanical materials). Treating these crystalline or semi-crystalline molecular materials under the influence of external perturbations requires a balanced description of subtle intermolecular forces. We show that the presented approaches provide CCSD(T)-quality results while appealing with reduced scaling with system size as low as O(N) as well as embarrassing parallelism. Different variants for the many-body embedding, ranging from point charges to quantum mechanical embedding, are analyzed with respect to the quality of the results and computational efficiency. We then present applications of our approaches to finding improved hydrogen-bonded organic piezoelectric materials [1-2]. We conclude with an outlook on excited states of metallic nanoparticles [3] and present our development of fast approaches for excited state calculations.

[1] K. A. Werling, G. R. Hutchison, and D. S. Lambrecht, “Piezoelectric Effects of Applied Electric Fields on Hydrogen-Bond Interactions: First-Principles Electronic Structure Investigation of Weak Electrostatic Interactions”, *J. Phys. Chem. Lett.* **4**, 1365-1370 (2013).

[2] K. A. Werling, M. Griffin, G. R. Hutchison, and D. S. Lambrecht, "Piezoelectric Hydrogen Bonding: Computational Screening for a Design Rationale", *J. Phys. Chem. A* **118**, 7404-7410 (2014).

[3] M. J. Hartmann, H. Häkkinen, J. E. Millstone, and D. S. Lambrecht, "Impacts of copper position on the electronic structure of $[Au_{25-x}Cu_x(SH)_{18}]^-$ nanoclusters", *J. Phys. Chem. C* **119**, 8290-8298 (2015).