TOWARD PREDICTIVE COMPUTATIONAL DESIGN OF PRECISION MOLECULAR OPTOELECTRONICS

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EXECUTIVE SUMMARY

We introduced and fully developed novel scalable algorithms and software for predictively accurate (ab initio) electronic structure calculations for the key electronic parameters (electron-detachment/attachment energies) of large conjugated molecules and solids—potential components of precision organic optoelectronic devices such as solar cells, light-emitting diodes, field-effect transistors, smart windows, and the like. We transformed the usual, nonscalable sum-of-products expressions of many-body Green’s function theories in the complete-basis-set limit into a few high-dimensional integrals, which were then evaluated by a highly scalable Metropolis Monte Carlo algorithm. They efficiently compute energy differences (including quasiparticle energy bands) directly without a sign problem, one of the major unsolved problems in the physics of many-particle systems, on many CPUs or many GPUs, easily achieving an unprecedented speedup by a factor of 31,000 (on 256 GPUs) systems, on many CPUs or many GPUs, easily achieving an unprecedented speedup by a factor of 31,000 (on 256 GPUs)

We are entering an exciting new era of chemical technology in which synthetic chemists can now fabricate complex solid-state materials made of organic components with precise dimensions, so that they display predicted/designed functions and performance as optoelectronic devices. The revolutionary impact of such devices requires no explanation. Miniaturizing components as many-body Green’s function (MBGF) theory (1). However, as compared with other ab initio theories, MBGF is less understood and developed, both theoretically and algorithmically. We aim to address this issue with the aid of Blue Waters.

METHODS & CODES

We mathematically transformed the usual sum-of-products expressions of second-order MBGF (GF2) theory and its complete-basis-set (CBS) correction by explicitly correlated (F12) ansätze into single high-dimensional integrals by a Laplace transform. These integrals (over 12-dimensional coordinates of two coupled electron pairs and one-dimensional imaginary time coordinate; see Fig. 1) are then evaluated by a Metropolis Monte Carlo method with judiciously chosen weight functions. The resulting stochastic methods—Monte Carlo GF2 (MC-GF2) [2] and Monte Carlo explicitly correlated GF2 (MC-GF2-F12) [3]—can compute energy differences (electron detachment/attachment energies) directly without a sign problem in a scalable manner with respect to both system size (the operation cost scales linearly per MC step and cubic-to-quartic scaling to achieve relative accuracy with negligible memory cost) [4]. The methods can also calculate quasiparticle energy bands of a solid for the entire Brillouin zone as nearly limit) GF2 calculation of electron-detachment energies of a wide range of large conjugated organic molecules (Fig. 2), many of which are used in an organic optoelectronic device. Note that the usual divide-and-conquer approach is powerless in treating such a delocalized property of a delocalized electronic structure. The largest calculation was performed on C60 with 1,610 basis functions and their capacity testing.

WHY BLUE WATERS

The stability and ease-of-use of Blue Waters, as well as the balanced deployment of CPUs and GPUs, are all essential for rapid coding/profiling of new scalable algorithms from scratch and their capacity testing.

PUBLICATIONS & DATA SETS