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TOWARD PREDICTIVE COMPUTATIONAL DESIGN OF PRECISION MOLECULAR OPTOELECTRONICS

Allocation: Blue Waters Professor/200 Knh
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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) relative to a serial calculation.

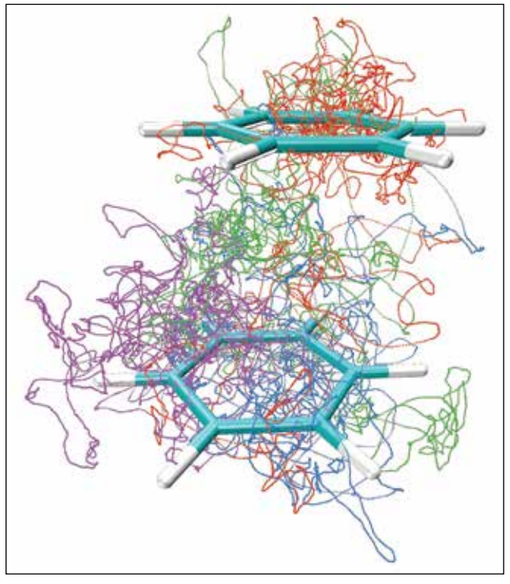

Figure 1: Imaginary-time evolution of electron-pair walkers in the benzene dimer.

RESEARCH CHALLENGE

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 for computing, light emission, memory, etc., by many orders of magnitude. Such a research program needs to be assisted by computational methods that can predict the key optoelectronic parameters of the component conjugated organic molecules such as electron-attachment/detachment energies, charge mobility, exciton binding, air stability, etc. A systematically accurate series of approximations for these properties in a molecule and solid exists 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 computer size (on thousands of CPUs or hundreds of GPUs) and 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 continuous curves of a wave vector [5], and have been extended to third-order MBGF [6] using an expedient interpretation of Brueckner–Goldstone diagrams as well as a convergence-acceleration scheme ("redundant-walker algorithm") [7].

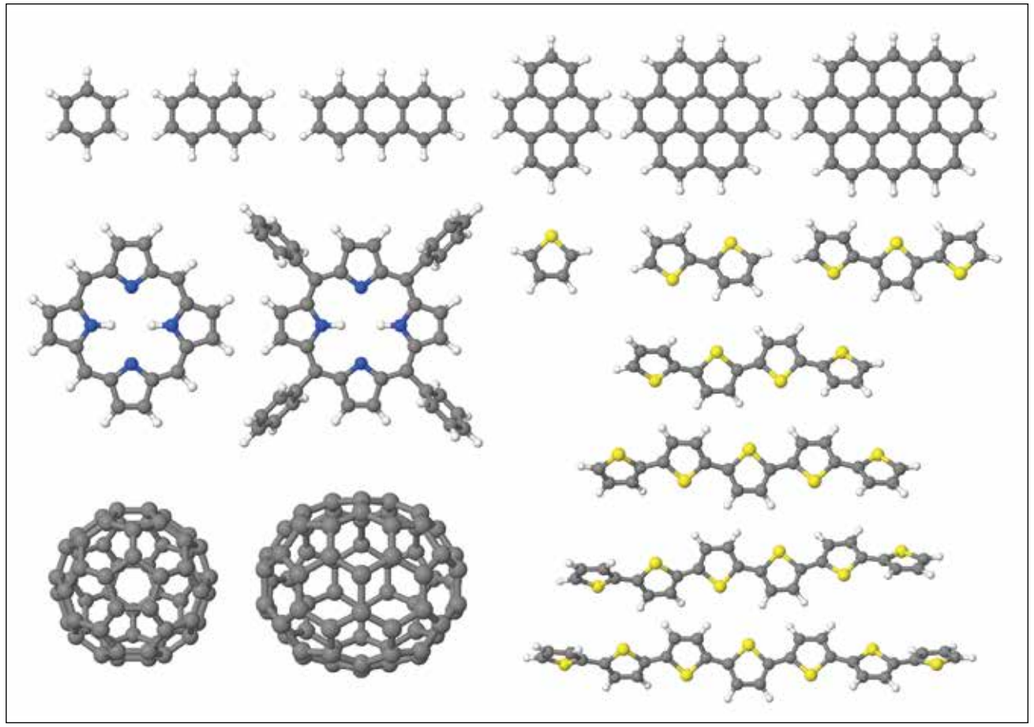

Figure 2: Molecular components of precision organic electronics devices studied.

RESULTS & IMPACT

We have developed the MC-GF2-F12 method that efficiently executes on both XE and XK nodes, enabling an exact (CBS-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 C_{70} with 1,610 basis functions using 128 GPUs for the GF2 portion and 896 CPUs for the F12 part. The result underscores the significance of including both electron-correlation and basis-set-extension effects because the Hartree–Fock calculation with a small basis set gives a deceptively accurate result by error cancellation.

The calculations were accelerated by the redundant-walker algorithm [7], which propagates more walkers than minimally necessary and permutes them in all possible ways when being substituted into the integrand, thereby multiplying the sampling efficiency. The MC-GF2 algorithm employs a two-level parallelism, in which dense matrix multiplications for many walkers are fine-grained on a GPU, and a Monte Carlo integration is coarse-grained across multiple CPU-GPUs, thereby enhancing the performance of the redundant-walker algorithm on GPUs beyond the degree that is possible by merely running on many CPUs [4].

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

Johnson, C.M., A.E. Doran, S.L. Ten-no, and S. Hirata, Monte Carlo explicitly correlated second-order many-body Green's function theory. To be submitted (2018).

Johnson, C.M., S. Hirata, S., and S. Ten-no, Explicit correlation factors. *Chem. Phys. Lett.*, 683 (2017), pp. 247–252.

Johnson, C.M., A.E. Doran, J. Zhang, E.F. Valeev, and S. Hirata, Monte Carlo explicitly correlated second-order many-body perturbation theory. *J. Chem. Phys.*, 145 (2016), p. 154115.

Doran, A.E., and S. Hirata, Monte Carlo MP2 on many graphical processing units. *J. Chem. Theory Comput.*, 12 (2016), pp. 4821–4832.