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TOWARD PREDICTIVE COMPUTATIONAL DESIGN OF PRECISION MOLECULAR OPTOELECTRONICS

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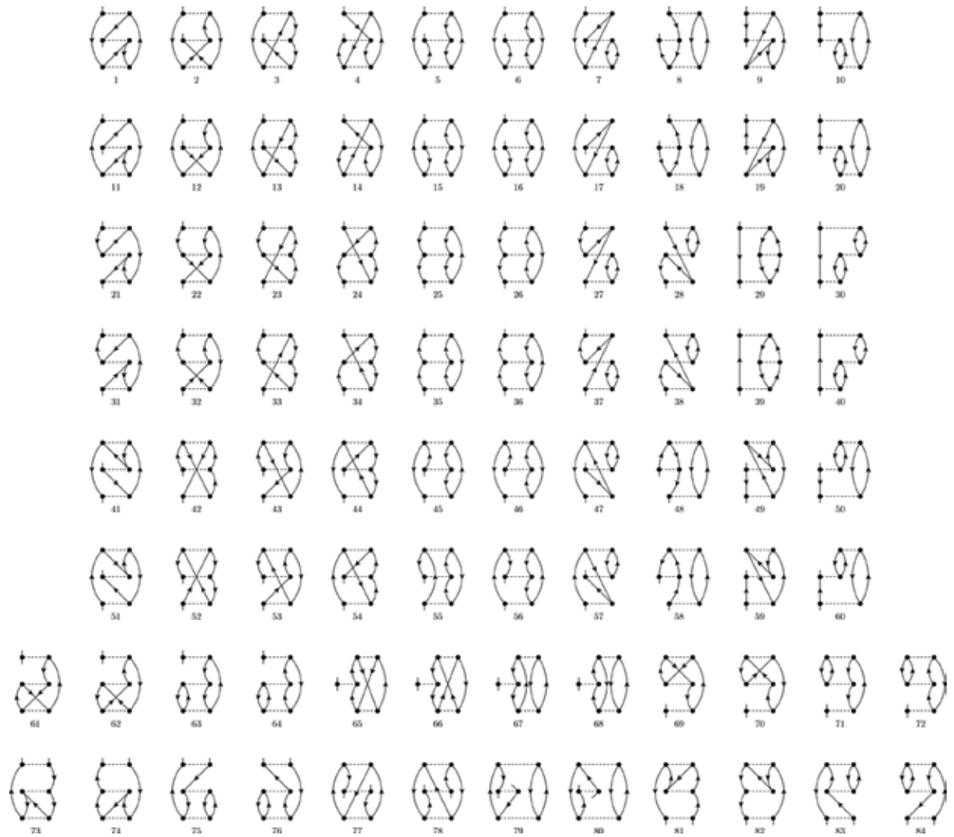
EXECUTIVE SUMMARY

The research team introduced and fully developed novel scalable algorithms and software for predictively accurate (*ab initio*) electronic-structure calculations for the key electronic parameters (electron binding energies) of large conjugated molecules and solids. These molecules and solids are potential components of precision organic optoelectronic devices such as solar cells, light-emitting diodes, field-effect transistors, smart windows, etc. The team transformed the usual nonscalable sum-of-products expressions of many-body Green's function theories into a few high-dimensional integrals, which were then evaluated by a highly scalable Metropolis Monte Carlo algorithm. The algorithm efficiently computes energy differences (including quasiparticle energy bands) directly without a sign problem on many CPUs or GPUs.



RESEARCH CHALLENGE

The world is 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 the fabricated materials display predicted/designed functions and performance as optoelectronic devices. The revolutionary impact of such devices requires no explanation as they will miniaturize components for computing, light emission, memory, and the like, by many orders of magnitude. Research into such technology may be assisted powerfully by computational methods that can predict the key optoelectronic parameters of the component conjugated organic molecules, such as electron binding 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 theory [1]. However, as compared with other *ab initio* theories, many-body Green's function theory is less well understood or developed both theoretically and algorithmically. The research group aims to address this issue with the assistance of Blue Waters.

METHODS & CODES

The team mathematically transformed the usual sum-of-products expressions of second- and third-order many-body Green's function—GF2 [2] and GF3 [3]—theories, and their complete-basis set correction by explicitly correlated *ansätze* [4] into single high-dimensional integrals by a Laplace transform. Specifically, in the last funding cycle, 84 Feynman diagrams defining GF3 (Fig. 1) [1] were automatically generated by symbolic computing software and transformed into algebraic formulas consisting of integrals over 20-dimensional coordinates of three coupled electron pairs and over two imaginary time coordinates. These were then evaluated by a Metropolis Monte Carlo method with judiciously chosen weight functions. The resulting stochastic GF2 and GF3 methods can directly compute energy differences (electron detachment/attachment energies) without a sign problem on thousands of CPUs [5] or hundreds of GPUs [6] with an unprecedented efficiency.

RESULTS & IMPACT

Supercomputers of the size and style of Blue Waters are changing the way chemical computing is being designed and performed. Conventional deterministic and matrix-algebra-based algorithms have given way to stochastic algorithms because of their superior parallel scalability on CPUs and GPUs; cost performance for high dimensions at the expense of having stochastic errors; naturally fault-tolerant and indefinitely restartable algorithms; and, finally and importantly, their relatively low human cost of code development. What the research team has achieved in this project is a paradigm of such changes in chemical computing.

WHY BLUE WATERS

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

PUBLICATIONS & DATA SETS

A. E. Doran and S. Hirata, "Monte Carlo second- and third-order many-body Green's function methods with frequency-dependent, non-diagonal self-energy, *J. Chem. Theory Comput.*, Oct. 2019, doi: 10.1021/acs.jctc.9b00693.

C. M. Johnson, A. E. Doran, S. L. Ten-no, and S. Hirata, "Monte Carlo explicitly correlated second-order many-body Green's function theory," *J. Chem. Phys.*, vol. 149, p. 174112, Nov. 2018, doi: 10.1063/1.5054610.

C. M. Johnson, S. Hirata, and S. Ten-no, "Explicit correlation factors," *Chem. Phys. Lett.*, vol. 683, pp. 247–252, Sept. 2017, doi: 10.1016/j.cplett.2017.02.072.

C. M. Johnson, A. E. Doran, J. Zhang, E. F. Valeev, and S. Hirata, "Monte Carlo explicitly correlated second-order many-body perturbation theory, *J. Chem. Phys.*, vol. 145, p. 154115, Oct. 2016, doi: 10.1063/1.4964854.

A. E. Doran and S. Hirata, "Monte Carlo MP2 on many graphical processing units," *J. Chem. Theory Comput.*, vol. 12, pp. 4821–4832, Oct. 2016, doi: 10.1021/acs.jctc.6b00588.

Figure 1 (opposite page): Eighty-four Feynman diagrams of the self-energy of third-order many-body Green's function theory, computer-generated and transformed into algebraic formulas convenient for Monte Carlo integration.