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Electronic Structure Theory for Photo-Induced Spin-Forbidden Dynamics

Toru Shiozaki
NORTHWESTERN UNIVERSITY

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14. ABSTRACT

Under this AFOSR Young Investigator award “Electronic Structure Theory for Photo-Induced Spin-Forbidden Dynamics” (FA9550-15-1-0031), we have developed novel electronic structure theory, algorithms, and programs for solving relativistic quantum mechanical equations based on the so-called Dirac equation. In addition, we have developed a computational tool for computing analytical nuclear forces and derivative couplings for the so-called complete active space second-order perturbation (CASPT2) methods. (more extensive abstract has been submitted together with this form)

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Final Report for FA9550-15-1-0031

Toru Shiozaki
Department of Chemistry, Northwestern University

Summary:

Under this AFOSR Young Investigator award "Electronic Structure Theory for Photo-Induced Spin-Forbidden Dynamics" (FA9550-15-1-0031), we have developed novel electronic structure theory, algorithms, and programs for solving relativistic quantum mechanical equations based on the so-called Dirac equation. Specific accomplishments include robust implementation of 4-component relativistic CASSCF programs, implementation of 4-component relativistic CASPT2 and MRCI, and their analogues for molecules under a magnetic field using gauge-including atomic orbitals. Our research has significantly advanced the state of the art, making these simulations routinely possible for sizable molecules consisting of up to 100 atoms with a few heavy element atoms (which was impossible prior to this research).

In addition, we have developed a computational tool for computing analytical nuclear forces and derivative couplings for the so-called complete active space second-order perturbation (CASPT2) methods. The implementation of CASPT2 nuclear gradients and derivative couplings was sought for more than two decades, and our work is the very first realization of such code since the CASPT2 model was developed in 1992. The code that we developed is parallelized and extremely efficient; we have demonstrated (in Mol. Phys. 2018) that simulation as large as retinal isomerization dynamics (54 atoms, CAS(12e, 12o)) can be performed using our program.

Based on these achievements, we have published eight research articles in top theoretical chemistry journals, acknowledging the generous support by DOD AFOSR. All of the code has been implemented in the program package called BAGEL, which is publicly available on a website. The number of users has gone up significantly in the past year; its user base is now estimated to be more than 50 research groups (and increasing) around the world, which attests to the large impact that our research has produced over the past three years.

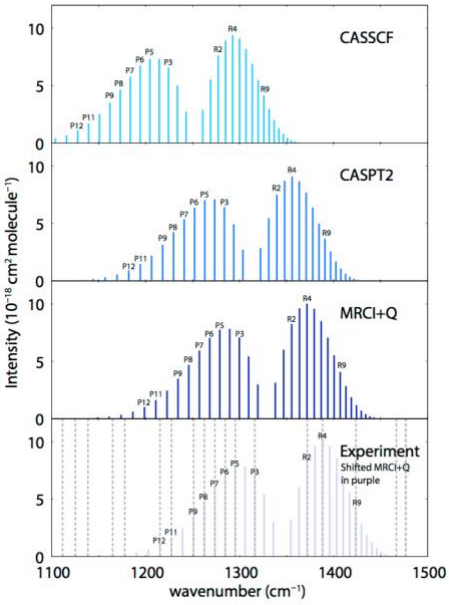

Figure 1: Rovibrational spectra of TlH computed by the fully relativistic methods that we have developed under this award.

Highlights:

(1) Relativistic quantum chemistry based on the Dirac equations.

Prior to our research, it was widely believed that, though most rigorous, four-component relativistic quantum mechanical equations (called the Dirac equation) cannot be solved accurately for molecules of chemical interest. In Ref. 2 below, we demonstrated that it is possible to apply these methods to

small molecules (Figure 1). The code has since then been parallelized and not it is possible to simulate large molecules with 100 atoms (to be published in the near future).

(2) CASPT2 nuclear forces, derivative couplings, and direct dynamics

We have address, under this award, the long-lasting technical challenges associated with the implementation of CASPT2 nuclear gradients and derivative couplings. The CASPT2 model was developed by Roos and coworkers back in the early 90s and it has been used by many computational chemists. However, the implementation of nuclear forces using this method had not been realized (prior to our report), mainly because of the enormous complexity of equations and implementation work. We have overcome this challenge by developing a program that performs derivation and generates a parallel code. We call the code generator SMITH3. The code has since been extended to multi-state variants and derivative coupling computations, each of which has been published in top theoretical chemistry journals acknowledging this grant. Over the past three years, it has gained a lot of attention from computational chemistry community, and our code is now being used by at least 50 research groups across the world. We ourselves have also demonstrated several numerical results in the literature. Figure 2 shows some of the trajectories in our study for non-radiative decay of a GFP model chromophore using the surface hopping on-the-fly dynamics methodologies together with the CASPT2 nuclear forces and derivative couplings developed in this research.

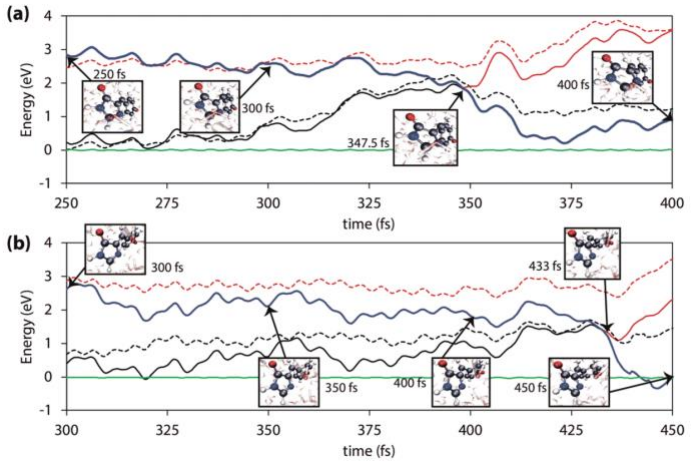

Figure 2: Examples of trajectories in on-the-fly surface hopping dynamics for a GFP model chromophore.

(3) An efficient, parallel electronic structure program package, BAGEL

All of the development outlined above has been implemented into a publicly available program package called BAGEL, which has been responsible for dissemination of the work. It has been licensed under the GNU General Public License and has been used by many computational chemists. The user manual can be found at https://nubakery.org, where the link to the source code (currently hosted at GitHub) is available.s

Articles that have acknowledged this funding:

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2. T. Shiozaki and W. Mizukami, Journal of Chemical Theory and Computation 11, 4733-4739 (2015), "Relativistic internally contracted multireference electron correlation methods"
3. B. Vlaisavljevich and T. Shiozaki, J. Chem. Theory Comput., 2016, 12 (8), pp 3781–3787. DOI: 10.1021/acs.jctc.6b00572. "Nuclear Energy Gradients for Internally Contracted Complete Active

Space Second-Order Perturbation Theory: Multistate Extensions"
4. T. Shiozaki and T. Yanai, J. Chem. Theory Comput., 2016, 12 (9), pp 4347–4351. DOI: 10.1021/acs.jctc.6b00646. "Hyperfine Coupling Constants from Internally Contracted Multireference Perturbation Theory"
5. J. W. Park and T. Shiozaki, Journal of Chemical Theory and Computation 13, 2561-2570 (2017), "Analytical derivative coupling for multistate CASPT2 theory"
6. J. W. Park and T. Shiozaki, Journal of Chemical Theory and Computation 13, 3676-3683 (2017), "On-the-fly CASPT2 surface hopping dynamics"
7. T. Shiozaki, WIREs Computational Molecular Science, 8, e1331 (2019), software focus, "BAGEL: Brilliantly Advanced General Electronic-structure Library"
8. J. W. Park and T. Shiozaki, *Molecular Physics* **116**, 2583–2590 (2018), special issue, "On the accuracy of retinal protonated Schiff base models"