JCTC Journal of Chemical Theory and Computation

Editorial

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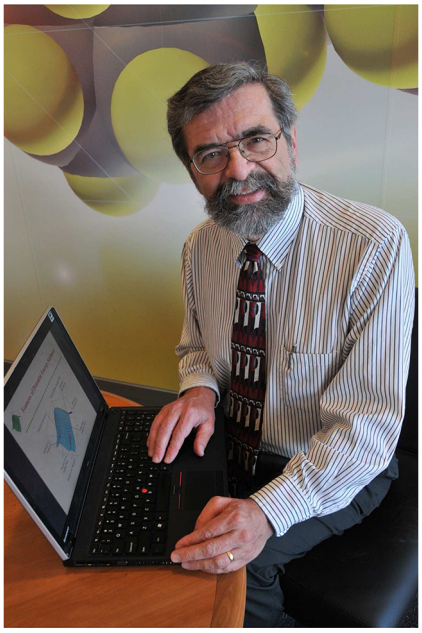
Thirty Years of Geometry Optimization in Quantum Chemistry and Beyond: A Tribute to Berny Schlegel



Photograph of H. Bernhard Schlegel courtesy Wayne State University

In the not-too-distant past, quantum chemistry was relegated to the limited purview of a small corps of experts. This is an essentially unbelievable picture for those of us trained in the past couple of decades. Indeed, much has changed. Today, quantum chemistry is a full fledged partner in advancing the chemical enterprise, used by experts and non-experts alike. This increase in use—realized over a relatively short time span—has certainly been aided by hardware advances that have yielded faster, smaller, and cheaper computers. For the field to arrive at its present state, though, advancements in theory and methods have also been critical. In particular, the present-day study of chemical events using computational quantum chemistry relies on both the advancement of accurate electronic structure models and robust methods for exploring potential energy surfaces (PESs).

This special issue of the *Journal of Chemical Theory and Computation* is dedicated to a leading figure in the study of PESs in quantum chemistry, H. Bernhard Schlegel. Together with a symposium honoring Berny Schlegel at the 244th ACS National Meeting (Philadelphia, PA), this issue specifically marks the 30th anniversary of the landmark "Berny Optimization" paper.[1]

Berny was born in Frankfurt, Germany, in 1951. His family moved to Canada when he was just four years old, and he grew up in Windsor, Ontario. With a strong interest in science and a Ford Motor Company scholarship in hand, he began undergraduate studies in chemical engineering at the University of Waterloo. During that time, Berny took an organic chemistry course by correspondence from Prof. Bert Fraser-Reid, who became his undergraduate research advisor and persuaded him to become a chemistry major.

After graduating from Waterloo in 1972, he began graduate studies at Queen's University in Kingston, Ontario. He pursued work in physical organic chemistry with Prof. Saul Wolfe. Initially, the thesis project was to involve both synthesis and electronic structure theory components. However, it was apparent early on that Berny's talents were best suited for the latter rather than the former, and his thesis project was quickly refocused entirely on computations. Guided by Pulay's seminal papers on Hartree–Fock (HF) gradient theory and the force method for determining force constants,[2−4] Berny independently wrote a program for evaluating analytic HF first derivatives. During this time, he developed an efficient approach for computing integral derivatives for basis sets comprised of s and p Cartesian Gaussian functions.[5] Because computing resources were limited at Queen's, Berny made numerous trips to Prof. Imre Csizmadia's lab at the University of Toronto to run calculations. Further computing cycles were found in Bologna, Italy, where Saul Wolfe sent Berny on several occasions as part of a fruitful collaboration with Prof. Fernando Bernardi. With Peter Pulay serving as an external examiner, Berny successfully defended his thesis in 1975.

Awarded an NRC–NATO postdoctoral fellowship, Berny moved to Princeton University to work with Profs. Kurt Mislow and Leland C. Allen. In 1976, he chose to continue his post-doctoral studies at Carnegie–Mellon University with Prof. John Pople. Working with Krishnan Raghavachari (then a student with John Pople), Berny made significant contributions in analytic derivative theory. One of the most notable papers from that time was the first affordable implementation of analytic HF second derivatives and MP2 first derivatives.[6] His work in Pittsburgh also included the implementation of an efficient geometry optimization program within GAUSSIAN, which the Pople group and others immediately put to good use dramatically expanding the relevance of electronic structure theory in chemistry.[7,8]

In 1978, Berny joined Merck, Sharp, and Dohme Research Laboratories, where he carried out molecular orbital calculations for guiding drug design. Two years later, he joined Wayne State University as an Assistant Professor of Chemistry. He rose through the ranks quickly, being promoted to Full Professor in 1986.

Shortly after beginning his academic career in Detroit, Berny prepared the manuscript honored in this Festschrift.[1] The paper documented the optimization program he had perfected over the previous few years. Submitted in 1981, "Optimization of Equilibrium Geometries and Transition Structures" described the method as implemented in the already released GAUSSIAN 80 suite of programs.[9] When viewed through the prism of Berny's graduate and postdoctoral work, the paper serves as a perfect culmination of a research program begun by Berny in the early 1970s. With the initial goal of studying the vibrational spectra of organic compounds, Berny developed an efficient integral

Special Issue: Berny Schlegel Festschrift

Published: December 11, 2012

   dx.doi.org/10.1021/ct300950r | *J. Chem. Theory Comput.* 2012, 8, 4853–4855

derivative scheme, implemented analytic HF first derivatives and the force method for computing force constants, and advanced analytic derivative theory for post-HF models. In that short time, he addressed all the essential ingredients of an economical and general algorithm for geometry optimization in quantum chemistry.

With more than 2300 citations, that paper is also representative of two critical advancements in general electronic structure theory that many of us take for granted today: (1) the combination of structure theory and PES exploration and (2) the application of quantum chemistry to the study of reactivity and mechanism. The Berny Optimizer was not the first attempt at finding stationary points on quantum chemistry energy landscapes, but it was unique in the care taken to balance the capabilities of the optimization procedure with the cost of evaluating the potential energy and its derivatives on-the-fly. As Berny wrote, a successful geometry optimization method in quantum chemistry must take "into account the special economics of ab initio calculations."[1] The genius of the method was the way it accounted for these unique economical factors. Coupled with the efficient methods developed by the Pople group and distributed in the GAUSSIAN program, the Berny optimizer opened the door for applications of computational quantum chemistry to a number of problems of interest in the broader chemistry community.

Since publishing the landmark work we honor here (Berny's 50th publication), another 300+ papers have appeared from Berny and his co-workers.[10] Extending the capabilities of geometry optimization, Berny has published some of the most highly cited works on coordinate transformations, force constant estimation, and transition structure optimization. His interests have also led to widely used methods for following reaction pathways and carrying out ab initio molecular dynamics calculations.

A hallmark of Berny's research is a strong interaction between methods development and theory applications to frontier chemical questions. An interest in studying the reactivity of organic radicals inspired the study of spin contamination and its effect on the quality of post-SCF calculations. In turn, Berny developed a series of spin projection methods, including the well-known PMP2 method. Investigations of reactions in protein active sites motivated methods work in efficient coordinate transformations and QM/MM geometry optimization. Challenged by a colleague to investigate how strong field lasers can control chemical reactivity, Berny recently began a new line of development in time dependent electronic structure theory.

Key to this interaction of theory and chemistry has been active collaborations with experimental groups. The number of experimental collaborators and the breadth of the chemistry investigated are spectacular, and there have been (and continue to be) too many to list. Perhaps showing that his roots are still in Saul Wolfe's laboratory, Berny is always excited to think about the chemistry when his group works with experimentalists. He is an equal partner in joint computational/experimental projects. Of course, these collaborative efforts also provide the fuel for Berny's next wave of method innovations.

By every metric and index, Berny's impact is significant.[11] In recent years, he has been recognized by a number of scientific organizations and academies. In 2011, Wayne State University named him University Distinguished Professor, the university's highest rank held by only 30 faculty across the campus.[12] He is a member of the Wayne State University Academy of Scholars and the International Academy of Quantum Molecular Science and is a fellow of the Royal Society of Chemistry, the American Association for the Advancement of Science, and the American Chemical Society. Most recently, Berny received the 2013 ACS Award for Computers in Chemical and Pharmaceutical Research. These honors and awards recognize not only Berny's impact on our field but also the service he has provided to the community, including his position as Associate Editor of this journal.

Over the past 30 years, Berny has established himself as a trusted authority on computational quantum chemistry and is one of the most respected members of our community. Former group members, colleagues, and friends—including many of the most recognizable names in computational chemistry—have joined us in honoring Berny by contributing to this Festschrift.

The two of us were students with Berny in the early 2000s. He is a mentor of the first degree, a constant advocate for his students and postdocs, and a trusted confidant. Every aspect of his character inspired us when we were students in Detroit and inspires us now as we carry on in our independent careers.

It is a true pleasure to bring this fitting tribute to fruition. We are thankful for the contributions to this issue by so many notable authors. Their participation speaks to their esteem for Berny's work and character. We are also grateful for the support Prof. Gustavo Scuseria (JCTC Editor in charge of this special issue) and his assistant Ms. Judy Jenkins provided for this project.

Finally, we thank Berny. His impact on the field brought us to his group, his scientific approach guided us as students, and his work today continues to inspire us. We cannot wait to see what problems he and the group will attack tomorrow!

■ ISSUE COVER PERMISSION STATEMENTS

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■ ASSOCIATED CONTENT

Supporting Information

The CV and a list of publications of H. Bernhard Schlegel. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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(7) By the time the Berny Optimization paper was published, more than 3000 molecules had been optimized and archived by Pople and co-workers. See the footnote on page 217 of ref 1.
(8) Whiteside, R. A.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*; Carnegie-Mellon University: Pittsburgh, PA, 1980.
(9) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahni, L. R.; Pople, J. A. *Gaussian 80*; Carnegie-Mellon University: Pittsburgh, PA, 1980.
(10) Berny Schlegel's complete publication list is included as Supporting Information.
(11) According to the ISI Web of Knowledge database, H. B. Schlegel's h-index is 75. In 2011, his indexed papers received 1753 citations. As of October 26, 2012, his indexed papers had received a total of 27 821 citations; 57 of his indexed papers have received at least 100 citations, and five of his indexed papers have received at least 1000 citations.
(12) The Distinguished Professor rank is held by less than 3% of Wayne State University's tenured and tenure-track faculty.