THE JOURNAL OF PHYSICAL CHEMISTRY A

 VOLUME 113, NUMBER 45, NOVEMBER 5, 2009

Tribute to Russell M. Pitzer

Herein, the career and accomplishments of Russell M. Pitzer in quantum-chemistry research are reviewed. His research extends from the small-molecule SCF era all the way to relativistic chemistry and the actinides, including the study of fullerenes and many large complexes. He has contributed extensively both to the methodology of quantum chemistry and to its applications and collaborated with experimental researchers to obtain theoretical data relevant to their research. Pitzer has played a key role in the establishment of the Ohio Supercomputer Center and contributed extensively to the development of the COLUMBUS program system, including its relativistic calculations capabilities. His work has been marked with elegance and meticulous execution.

1. The Early Years

Russell (Russ) M. Pitzer was born on May 10, 1938 in Berkeley, California. His grandfather, orange grower Russell K. Pitzer (1878−1978), founded Pitzer College, one of the seven "Claremont Colleges" that constitute the Claremont University Consortium. His father was the eminent Berkeley physical chemist Kenneth S. Pitzer (1914−1997). Following in his father's footsteps, Russ has served since 1988 as a trustee of Pitzer College and received an honorary degree of Doctor of Humane Letters from the college in 2008.

Russ attended the California Institute of Technology, where, in addition to earning a B.S. degree with academic honors in chemistry in 1959, he played guard and tackle positions on the

10.1021/jp9085393 CCC: $40.75
Published on Web 11/05/2009

Caltech football team. Because of a shortage of experienced players at Caltech, he played on both the offense and defense teams. A highlight of his football career was a game against Occidental College in the Rose Bowl, in which he was a "trap blocker" in a 12-yard scoring play.

For his graduate studies, Russ went to Harvard, where he earned an A.M. in physics (1961) and a Ph.D. in chemical physics (1963), working with William N. Lipscomb. An early part of this research involved the calculation of multicenter integrals for Slater-type orbitals (STOs)[1] using the expansion of an STO on one center in terms of similar functions on another center, similarly to the approach of Barnett and Coulson.[2] This work was the beginning of a long-lasting interest in the efficient calculation of multicenter integrals, although subsequent efforts mostly involved contracted Gaussian-type orbitals, the current standard in ab initio quantum chemistry.

An important contribution[3] from his graduate work at Harvard was the formulation of the coupled-perturbed-Hartree−Fock (HF) equations that determine the change in a basis-set expanded HF (Hartree−Fock−Roothaan, or SCF) wave function under the effects of a perturbation. Another important contribution[4] from that period was an early detailed calculation of the internal rotation barrier in ethane, including an examination of various proposed origins of the barrier. He came back to this question later at Caltech,[5] which resulted in a convincing explanation of the origin of the barrier in terms of exclusion effects between the back-lobes of the sp^3 hybrid localized orbital of one methyl group and those of the other group.[6]

Pitzer returned to Caltech in 1963 as Noyes Research Instructor and then as assistant professor of chemistry. During this period, in addition to the above-mentioned work on the internal-rotation barrier in ethane, he carried out a series of molecular SCF calculations,[7−11] emphasizing the determination of molecular properties.

2. The Ohio State University

Pitzer came to Ohio State in 1968, with occasional association with Battelle Memorial Institute. His initial research at OSU continued his work on SCF calculations of small molecules and their properties,[12−16] and the study of internal-rotation barriers.[17−19] He also developed procedures for the efficient use of symmetry in molecular SCF calculations[20−22] and in the calculation and processing of molecular integrals,[23,24] including the integrals needed for the determination of molecular properties,[25] and the formulation of the equal-contribution theorem, which states that atomic orbital integrals related by symmetry contribute equally to symmetry orbital integrals whose integrands are totally symmetric.[23] Another interesting contribution was the development of an SCF method for hole states.[26] His molecular calculations now expanded to the study of larger molecules[27] and open-shell and excited states and their geometrical structures,[28−31] including interesting studies of trimethylenemethane[32,33] and its derivatives.[34,35] Such calculations often required post-SCF methods, such as MCSCF, usually in the generalized valence-bond form,[28,29] or CI.[30]

At this point, his interests turned to the special challenges of transition metal compounds with their many close-lying, open-shell states and varied geometrical structures,[36−40] including sandwich compounds such as $Ni(C_2H_4)_2$, $Ni(C_2H_4)_3$,[39] and $Ni(C_4H_4)_2$.[40] These studies were marked by the use of large and carefully optimized basis sets of contracted Gaussian-type orbitals and detailed study and optimization of molecular geometries. Another area of interest sparked by some of these studies involved the Jahn−Teller[37] and Renner−Teller[41] effects, an interest that continues to this day.

Other lines of research included the study of the structure and properties of beryllium atom clusters of various sizes,[42−48] from Be_{13} to Be_{135}, as successively better models for metallic beryllium,[47] and the study of transition metal impurities in crystals.[49−54]

3. The Ohio Supercomputer Center

The calculations on ever bigger and more complex systems would not have been possible without the appearance of supercomputers and the access provided to them. In the mid-1980s the National Science Foundation proposed to fund three national supercomputer centers for use by the U.S. scientific research community. Proposals for hosting such a center were submitted by several institutions, including a proposal from The Ohio State University at the initiative of three theoretical chemistry professors: C. William McCurdy, Russell M. Pitzer, and Isaiah Shavitt. When this proposal failed to get NSF support, the three initiators refocused their effort, with the support of the university president Edward H. Jennings, on an alternative project: a state-funded supercomputer center for the State of Ohio. This center was to provide supercomputing facilities for all academic institutions and state government units in the state and also allow access to industry on a cost-recovery basis. Pitzer took the initiative in mobilizing statewide support for the project, promoting a plan to establish a communications network to ease access to the center by the participating institutions. His tireless effort, as well as McCurdy's activities on the political front, succeeded in obtaining the support of the Ohio Board of Regents, key legislature members, and Governor Richard F. Celeste.

The Ohio Supercomputer Center was established in early 1987, and its first computer, a leased Cray X-MP2, was delivered on June 1 of that year. After a testing period, a formal dedication was held on November 2, 1987. Pitzer served as interim associate director and later interim director of the center and as chairman of the Statewide Users Group and was responsible for running the communications network. This center has been providing ever-improving computer power since then and has facilitated many of the advanced research projects that Pitzer and other researchers could undertake as a result.

4. The COLUMBUS Quantum-Chemistry Programs

Another key element in facilitating the detailed study of larger molecules, excited states, radicals, etc. was the development of the COLUMBUS system of programs for electronic structure calculations.[55−58] The principal objective of these programs was to allow multireference direct-CI calculations by the graphical unitary-group approach, but the initial stages of these programs were provided by Pitzer. These stages included an elegant input module for specifying the molecular geometry, symmetry, and basis set with a minimal amount of input, an integral calculation module for contracted Gaussian-type orbitals for both energy and property integrals, and an efficient SCF program. Later,[56] Pitzer contributed to the optimization and parallelization of these programs and to the addition of other capabilities, including the efficient use of generally contracted Gaussian basis sets, the use of effective core potentials, density matrix calculations for the evaluation of molecular electronic properties, and analytic calculation of gradients and other derivatives of the potential energy surface. Later work[57] provided analytic gradient calculations for several multireference wave function models, evaluation of spin−orbit integrals,[59] and spin−orbit CI calculations[60] in which the spin−orbit interaction is not treated as a perturbation but is part of the relativistic Hamiltonian. These enhance-

ments greatly expanded the usefulness and scope of the COLUMBUS program system.

5. Relativistic Chemistry and the Actinides

As the studies extended to molecules containing heavier atoms, it was becoming necessary to account for relativistic effects. Pitzer developed methods to incorporate such effects[61] using relativistic core potentials, double-group treatments of spatial symmetry, and spin−orbit CI, initially as a stand-alone CI program and later as part of the enhanced COLUMBUS programs.[57] These methods were applied in studies of molecules containing heavy atoms, including lanthanides and actinides. Among these were calculations on uranocene[62] ($U(C_8H_8)_2$), niobium, tantalum, hahnium (element 105), and their oxides;[63] dimolybdenum[64] and dirhenium[65] complexes; cerocene and thorocene;[66] and actinocenes and actinofullerenes.[67] To facilitate such calculations, Pitzer optimized basis sets for use with relativistic effective-core potentials.[68,69]

After fullerene, the C_{60} cage compound, was discovered in 1985, Pitzer carried out electronic structure calculations on C_{60} and its ionic and excited states[70] and on various lanthanide and actinide atoms inside C_{28} and $C_{28}H_4$ cage compounds, including $Hf@C_{28}$,[71,72] $Hf@C_{28}H_4$,[73] $Pa@C_{28}$, and $U@C_{28}$.[74] These were followed by further studies of the electronic states and spectra of actinide molecules, including actinyl ions,[75−79] uranyl and neptunyl ions in the $Cs_2UO_2Cl_4$ crystal environment,[80] UO_2F_2,[81] and actinides and their ions.[82]

6. Other Recent Work

Recently, Pitzer studied potential energy surface crossings involving the Jahn−Teller effect, with the silver trimer as a primary example.[83,84] He also investigated the binding energies of I^- and Xe with decaborane[85] and carried out *R*-matrix calculations for radiative transitions and photoionization for many high-*Z* elements to determine cross sections and attenuation coefficients for use in cancer diagnostics and therapeutics by embedding high-*Z* nanoparticles in tumors.[86]

Another focus of recent research has concerned automatic code-generation for quantum-chemistry computer programs, optimized for parallel computers, particularly for coupled-cluster calculations.[87,88]

7. Summary

It is clear from the preceding record of research and accomplishments that Russell M. Pitzer is a very versatile scientist, contributing to both methodology and applications across the spectrum of the quantum chemistry discipline. Much of his work has involved collaboration with experimental researchers, with the aim of answering specific needs for chemical knowledge. His work has been marked with elegance, careful attention to details, and meticulous execution, and his results have stood the test of time. It is a pleasure to congratulate him for his achievement on the occasion of the publication of this special issue of the Journal.

References and Notes

(1) Pitzer, R. M.; Kern, C. W.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 267.
(2) Barnett, M. P.; Coulson, C. A. *Philos. Trans. R. Soc. (London)* **1951**, *A 243*, 221.
(3) Stevens, R. M.; Pitzer, R. M.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *38*, 550.
(4) Pitzer, R. M.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *39*, 1995.
(5) Pitzer, R. M. *J. Chem. Phys.* **1967**, *47*, 965.
(6) Sovers, O. J.; Kern, C. W.; Pitzer, R. M.; Karplus, M. *J. Chem. Phys.* **1968**, *49*, 2592.
(7) Flygare, W. H.; Pochan, J. M.; Kerley, G. I.; Caves, T.; Karplus, M.; Aung, S.; Pitzer, R. M.; Chan, S. I. *J. Chem. Phys.* **1966**, *45*, 2793.
(8) Aung, S.; Pitzer, R. M.; Chan, S. I. *J. Chem. Phys.* **1966**, *45*, 3457.
(9) Palke, W. E.; Pitzer, R. M. *J. Chem. Phys.* **1967**, *46*, 3948.
(10) Pitzer, R. M. *J. Chem. Phys.* **1967**, *46*, 4871.
(11) Aung, S.; Pitzer, R. M.; Chan, S. I. *J. Chem. Phys.* **1968**, *49*, 2071.
(12) Pitzer, R. M.; Merrifield, D. P. *J. Chem. Phys.* **1970**, *52*, 4782.
(13) Dunning, T. H., Jr.; Pitzer, R. M.; Aung, S. *J. Chem. Phys.* **1972**, *57*, 5044.
(14) Bowers, M. J. T.; Pitzer, R. M. *J. Chem. Phys.* **1973**, *59*, 163.
(15) Yates, J. H.; Pitzer, R. M. *J. Chem. Phys.* **1977**, *66*, 3592.
(16) Grow, D. T.; Pitzer, R. M. *J. Chem. Phys.* **1977**, *67*, 4019.
(17) Kern, C. W.; Pitzer, R. M.; Sovers, O. J. *J. Chem. Phys.* **1974**, *60*, 3583.
(18) Winter, N. W.; Pitzer, R. M. *J. Chem. Phys.* **1975**, *62*, 1269.
(19) Pitzer, R. M. *Acc. Chem. Res.* **1983**, *16*, 207.
(20) Winter, N. W.; Ermler, W. C.; Pitzer, R. M. *Chem. Phys. Lett.* **1973**, *19*, 179.
(21) Pitzer, R. M. *J. Chem. Phys.* **1973**, *59*, 3308.
(22) Pitzer, R. M. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: New York, 1998; p 2929.
(23) Pitzer, R. M. *J. Chem. Phys.* **1973**, *58*, 3111.
(24) Power, J. D.; Pitzer, R. M. *Chem. Phys. Lett.* **1974**, *24*, 478.
(25) Pitzer, R. M. *J. Chem. Phys.* **1969**, *51*, 3191.
(26) Hsu, H.-L.; Davidson, E. R.; Pitzer, R. M. *J. Chem. Phys.* **1976**, *65*, 609.
(27) Scamehorn, C. A.; Hermiller, S. M.; Pitzer, R. M. *J. Chem. Phys.* **1986**, *84*, 833.
(28) Dunning, T. H., Jr.; White, W. P.; Pitzer, R. M.; Mathews, C. W. *J. Mol. Spectrosc.* **1979**, *75*, 297.
(29) White, W. P.; Pitzer, R. M.; Mathews, C. W.; Dunning, T. H., Jr. *J. Mol. Spectrosc.* **1979**, *75*, 318.
(30) de Castro, S. C.; Schaefer, H. F., III.; Pitzer, R. M. *J. Chem. Phys.* **1981**, *74*, 550.
(31) Murphy, R.; Schaefer, H. F., III.; Nobes, R. H.; Radom, L.; Pitzer, R. M. *Int. Rev Phys. Chem.* **1986**, *5*, 229.
(32) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1978**, *100*, 2227.
(33) Hood, D. M.; Schaefer, H. F., III.; Pitzer, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 8009.
(34) Auster, S. B.; Pitzer, R. M.; Platz, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 3812.
(35) Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 2245.
(36) Hsu, H.-L.; Peterson, C.; Pitzer, R. M. *J. Chem. Phys.* **1976**, *64*, 791.
(37) Yates, J. H.; Pitzer, R. M. *J. Chem. Phys.* **1979**, *70*, 4049.
(38) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1979**, *71*, 705.
(39) Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 7176.
(40) Pitzer, R. M.; Goddard, J. D.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 5681.
(41) Lee, T. J.; Fox, D. J.; Schaefer, H. F., III.; Pitzer, R. M. *J. Chem. Phys.* **1984**, *81*, 356.
(42) Ermler, W. C.; Kern, C. W.; Pitzer, R. M.; Winter, N. W. *J. Chem. Phys.* **1986**, *84*, 3937.
(43) Ross, R. B.; Ermler, W. C.; Pitzer, R. M.; Kern, C. W. *Chem. Phys. Lett.* **1987**, *134*, 115.
(44) Ermler, W. C.; Ross, R. B.; Kern, C. W.; Pitzer, R. M.; Winter, N. W. *J. Phys. Chem.* **1988**, *92*, 3042.
(45) Ross, R. B.; Kern, C. W.; Pitzer, R. M.; Ermler, W. C.; Winter, N. W. *J. Phys. Chem.* **1990**, *94*, 7771.
(46) Ross, R. B.; Ermler, W. C.; Luana, V.; Pitzer, R. M.; Kern, C. W. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1990**, *24*, 225.
(47) Ross, R. B.; Ermler, W. C.; Kern, C. W.; Pitzer, R. M. *Int. J. Quantum Chem.* **1992**, *41*, 733.
(48) Ross, R. B.; Kern, C. W.; Pitzer, R. M.; Ermler, W. C. *Int. J. Quantum Chem.* **1995**, *55*, 393.
(49) Winter, N. W.; Pitzer, R. M. In *Tunable Solid-Sate Lasers*; Hammerling, P., Budgor, A. B., Pinto, A., Eds.; Springer: Berlin,1985; p 164.
(50) Winter, N. W.; Pitzer, R. M.; Temple, D. K. *J. Chem. Phys.* **1987**, *86*, 3549.
(51) Winter, N. W.; Pitzer, R. M.; Temple, D. K. *J. Chem. Phys.* **1987**, *87*, 2945.
(52) Winter, N. W.; Pitzer, R. M. *J. Chem. Phys.* **1988**, *89*, 446.
(53) Luana, V.; Florez, M.; Recio, J. M.; Pueyo, L.; Bermejo, M.; Pitzer, R. M. *Radiat. Eff. Defects Solids* **1991**, *119−121*, 287.
(54) Winter, N. W.; Temple, D. K.; Luana, V.; Pitzer, R. M. *Adv. Mol. Electron. Struct. Theory* **1994**, *2*, 61.

(55) Lischka, H.; Shepard, R.; Brown, F. B.; Shavitt, I. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1981**, *15*, 91.
(56) Shepard, R.; Shavitt, I.; Pitzer, R. M.; Comeau, D. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J.-G. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1988**, *22*, 149.
(57) Lischka, H.; Shepard, R.; Pitzer, R. M.; Shavitt, I.; Dallos, M.; Müller, T.; Szalay, P. G.; Seth, M.; Kedziora, G. S.; Yabushita, S.; Zhang, Z. *Phys. Chem. Chem. Phys.* **2001**, *3*, 664.
(58) See http://www.univie.ac.at/columbus/ for information and references on the COLUMBUS program system.
(59) Pitzer, R. M.; Winter, N. W. *Int. J. Quantum Chem.* **1991**, *40*, 773.
(60) Yabushita, S.; Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*, 5791.
(61) Pitzer, R. M.; Winter, N. W. *J. Phys. Chem.* **1988**, *92*, 3061.
(62) Chang, A. H. H.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500.
(63) Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. *J. Phys. Chem.* **1993**, *97*, 5852.
(64) Blaudeau, J.-P.; Pitzer, R. M. *J. Phys. Chem.* **1994**, *98*, 4575.
(65) Blaudeau, J.-P.; Ross, R. B.; Pitzer, R. M.; Mougenot, P.; Bénard, M. *J. Phys. Chem.* **1994**, *98*, 7123.
(66) Dolg, M.; Fulde, P.; Stoll, H.; Preuss, H.; Chang, A.; Pitzer, R. M. *Chem. Phys.* **1995**, *195*, 71.
(67) Chang, A. H. H.; Zhao, K.; Ermler, W. C.; Pitzer, R. M. *J. Alloys Compd.* **1994**, *213/214*, 191.
(68) Wallace, N. M.; Blaudeau, J. P.; Pitzer, R. M. *Int. J. Quantum Chem.* **1991**, *40*, 789.
(69) Blaudeau, J. P.; Brozell, S. R.; Matsika, S.; Zhang, Z.; Pitzer, R. M. *Int. J. Quantum Chem.* **2000**, *77*, 516.
(70) Chang, A. H. H.; Ermler, W. C.; Pitzer, R. M. *J. Phys. Chem.* **1991**, *95*, 9288.
(71) Tuan, D. F.-T.; Pitzer, R. M. *J. Phys. Chem.* **1995**, *99*, 9762.
(72) Tuan, D. F.-T.; Pitzer, R. M. *J. Phys. Chem.* **1995**, *99*, 15069.
(73) Tuan, D. F.-T.; Pitzer, R. M. *J. Phys. Chem.* **1996**, *100*, 6277.
(74) Zhao, K.; Pitzer, R. M. *J. Phys. Chem.* **1996**, *100*, 4798.
(75) Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*, 6880.
(76) Matsika, S.; Pitzer, R. M. *J. Phys. Chem. A* **2000**, *104*, 4064.
(77) Matsika, S.; Pitzer, R. M.; Reed, D. T. *J. Phys. Chem. A* **2000**, *104*, 11983.
(78) Matsika, S.; Zhang, Z.; Brozell, S. R.; Blaudeau, J.-P.; Wang, Q.; Pitzer, R. M. *J. Phys. Chem. A* **2001**, *105*, 3825.
(79) Santos, M.; de Matos, A. P.; Marçalo, J.; Gibson, J. K.; Haire, R. G.; Tyagi, R.; Pitzer, R. M. *J. Phys. Chem. A* **2006**, *110*, 5751.
(80) Matsika, S.; Pitzer, R. M. *J. Phys. Chem. A* **2001**, *105*, 637.
(81) Wang, Q.; Pitzer, R. M. *J. Phys. Chem. A* **2001**, *105*, 8370.
(82) Gibson, J. K.; Haire, R. G.; Marçalo, J.; Santos, M.; Leal, J. P.; de Matos, A. P.; Tyagi, R.; Mrozik, M. K.; Pitzer, R. M.; Bursten, B. E. *Eur. Phys. J. D* **2007**, *45*, 133.
(83) Sioutis, I.; Stakhursky, V. L.; Pitzer, R. M.; Miller, T. A. *J. Chem. Phys.* **2007**, *126*, 124308.
(84) Sioutis, I.; Stakhursky, V. L.; Pitzer, R. M.; Miller, T. A. *J. Chem. Phys.* **2007**, *126*, 124309.
(85) Sioutis, I.; Pitzer, R. M. *J. Phys. Chem. A* **2006**, *110*, 12528.
(86) Pradhan, A.; Nahar, S.; Montenegro, M.; Sur, C.; Mrozik, M.; Pitzer, R.; Silver, E.; Yu, Y. *Med. Phys.* **2008**, *35*, 2718.
(87) Baumgartner, G.; Auer, A.; Bernholdt, D.; Bibireata, A.; Choppella, V.; Cocorvia, D.; Gao, X.; Harrison, R. J.; Hirata, S.; Krishnamoorthy, S.; Krishnan, S.; Lam, C.-C.; Lu, Q.; Nooijen, M.; Pitzer, R. M.; Ramanujam, J.; Sadayappan, P.; Sibiryakov, A. *Proc. IEEE* **2005**, *93*, 276.
(88) Auer, A. A.; Baumgartner, G.; Bernholdt, D.; Bibireata, A.; Choppella, V.; Cocorvia, D.; Gao, X.; Harrison, R.; Hirata, S.; Krishnamoorthy, S.; Krishnan, S.; Lam, C.-C.; Lu, Q.; Nooijen, M.; Pitzer, R.; Ramanujam, J.; Sadayappan, P.; Sibiryakov, A. *Mol. Phys.* **2006**, *104*, 211.

Isaiah Shavitt

University of Illinois

JP9085393