Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

ELSEVIER

CHEMICAL PHYSICS LETTERS

Historical perspective on: A fifth-order perturbation comparison of electron correlation theories [Volume 157, Issue 6, 26 May 1989, Pages 479–483]

CrossMark

Krishnan Raghavachari [*]

Department of Chemistry, Indiana University, Bloomington, IN 47405, USA

Summary by Krishnan Raghavachari, Nobel prize-winner: Professor John A. Pople.

The development of an accurate and cost-effective theory of electron correlation has been a major goal of quantum chemistry for decades. In 1989, we proposed a method [1], termed CCSD(T), which provided a novel perturbative treatment of the effects of triple excitations to augment the popular coupled cluster singles and doubles (CCSD) model [2,3]. More than two decades later, it still stands as the method of choice for accurate quantum chemical applications. It provides a consistently accurate description of chemical interaction strengths ranging from the strong multiple bonding in N_2 to the weak van der Waals interaction in He_2 [4]. Its combination of accuracy and applicability makes it a uniquely suitable method for a wide variety of molecules [5–7], and it has been termed as the 'Gold Standard' of quantum chemistry [8].

There are three important ingredients that led to the development of the CCSD(T) method in 1989. The first ingredient was the realization that the effects of triple excitations are vital to any quantitatively accurate treatment of electron correlation [9–11]. However, a straightforward evaluation using a method such as CCSDT is prohibitively expensive, involving iterative $O(N^8)$ steps. The second ingredient was the idea of a perturbative and non-iterative treatment of the effects of triple excitations [12,13]. The first such method, termed CCD+ST(CCD) [12], involved an evaluation of the effects of triples (and singles) in a manner analogous to fourth order perturbation theory, but using the converged CCD wavefunction instead of the first order wavefunction. This is extremely important to reduce the scaling of the triples evaluation to a single $O(N^7)$ step. The third ingredient was the realization that in an extension to CCSD, two separate contributions of triples should be included, one each resulting from their interaction with singles and doubles [14,15]. In other words, the triples have to be treated 'as a perturbation on a solution already obtained at the singles-doubles level' [14]. This idea is exactly analogous to that used earlier for the inclusion of triples in the QCISD(T) method [14]. While the contribution arising from singles is usually small numerically, it frequently has an opposite sign to the dominant doubles term, and provides stability in many difficult examples. A similar perspective has been offered by Stanton [16] who

indicates that 'these two terms should be treated together in formulating a balanced noniterative correction to CCSD'. In our original Letter [1], we used a detailed analysis of fifth order perturbation theory to justify the proposed approach. The method, labeled CCSD(T), was proposed and published in *Chemical Physics Letters* in 1989 [1]. As mentioned earlier, the method has become highly successful and our Letter has received over 4000 citations.

The excellent performance of the CCSD(T) method for challenging chemical problems [17] has been the foundation for many key applications in quantum chemistry. An important component here is the extrapolation of the results to the 'complete basis set' limit [4,18]. The resulting CCSD(T)/CBS energies [19] have proven to be remarkably accurate and have given rise to a variety of highly accurate thermochemical approaches that attain 'chemical accuracy'. For example, the G4 [20], W_{1-2} [21] and ccCA [22] thermochemical protocols rely on the inherent accuracy of the CCSD(T) correlation treatment. Even more interestingly, in some cases where higher excitations have been carefully analyzed, some cancellation of the effects of higher order triples and quadruples have been noted. In other words, the CCSDT method, while computationally intensive, is not always more accurate than CCSD(T).

More recently, there has been substantial interest in the treatment of weak interactions [23]. The CCSD(T) method is now so widely accepted that many authors use the CCSD(T)/CBS results instead of the experimental values to calibrate other theoretical treatments. For example, in the recent extended S66 test set for weak interactions [24], the energies of molecules at geometries displaced from their equilibrium values are also used to assess the accuracy of newly developed methods and density functionals. Much of this information on the test set comes from CCSD(T)/CBS calculations on such molecules at displaced geometries.

While the CCSD(T) method has enjoyed remarkable success, any such perturbative treatment will have its limitations and has to be assessed in comparison to more accurate methods. In this context, higher excitation terms such as full CCSDT, CCSDTQ and CCSDTQ5 terms have been incorporated in some thermochemical methods such as HEAT [25] or W4 [26]. Nevertheless, the sustained success of the CCSD(T) method even after more than two decades has been extremely gratifying to all the authors of our original Letter.

This special issue honors Nobel Laureates and their publications in *Chemical Physics Letters*. Sadly, Professor Sir John Pople, a pioneer

[*] Corresponding author.
  E-mail address: kraghava@indiana.edu

and dominant figure in the world of quantum chemical developments for decades, Nobel Laureate in Chemistry in 1998, Knighted by the British Empire in 2003, and my Ph.D. mentor with whom I continued to collaborate for more than two decades after my graduation, passed away in 2004. In the context of the current summary, Professor Pople has made numerous key contributions to the developments of electron correlation techniques in quantum chemistry. Particularly noteworthy are his contributions to Møller–Plesset perturbation theory (MP2–MP5) [27–32,10], quadratic configuration interaction (QCISD) [14], and coupled cluster theory (CCD) [33]. Among the most successful applications of these methods are the thermochemical treatments, G1–G3 theories [34–40] (and their variants), that set the challenging target of attaining chemical accuracy using computational methods. While the theoretical ideas and mathematical formulae for the perturbative treatment of the effects of triple excitations in QCISD(T) [14] and CCSD(T) [1] were my contributions, it was Professor Pople's suggestion to present them in the context of an expansion involving fifth-order perturbation theory. Clearly, the success of the CCSD(T) method and its broad acceptance by the entire quantum chemical community can be seen by the large number of groups that use the method, the many different software suites where the method has been implemented, and the ever-increasing number of citations for our Letter published in *Chemical Physics Letters* in 1989 (300 citations in 2012, and more than 4000 citations overall). I dedicate this summary to the memory of my advisor and scientific mentor, Professor Sir John Pople.

References

[1] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[2] R.J. Bartlett, M. Musial, Rev. Mod. Phys. 79 (2007) 291.
[3] G.D. Purvis, R.J. Bartlett, J. Chem. Phys. 76 (1982) 1910.
[4] T.H. Dunning, J. Phys. Chem. A 104 (2000) 9062.
[5] T.J. Lee, G.E. Scuseria, in: S.R. Langhoff (Ed.), Electronic Structure Calculations with Chemical Accuracy, Kluwer Academic Publishers, Dordrecht, 1995. p. 47.
[6] T. Helgaker, J. Gauss, P. Jorgensen, J. Olsen, J. Chem. Phys. 106 (1997) 6430.
[7] D. Feller, K.A. Peterson, D.A. Dixon, J. Chem. Phys. 129 (2008) 204105.
[8] See for example, J. Rezac, P. Hobza, J. Chem. Theory Comput. 9 (2013) 2151.
[9] S. Wilson, V.R. Saunders, J. Phys. B 12 (1979) 403. Erratum ibid. 13, 1505.
[10] R. Krishnan, M.J. Frisch, J.A. Pople, J. Chem. Phys. 72 (1980) 4244.
[11] R.J. Bartlett, H. Sekino, G.D. Purvis, Chem. Phys. Lett. 98 (1983) 66.
[12] K. Raghavachari, J. Chem. Phys. 82 (1985) 4607.
[13] M. Urban, J. Noga, S.J. Cole, R.J. Bartlett, J. Chem. Phys. 83 (1985) 4041.
[14] J.A. Pople, M. Head-Gordon, K. Raghavachari, J. Chem. Phys. 87 (1987) 5968.
[15] Y.S. Lee, S.A. Kucharski, R.J. Bartlett, J. Chem. Phys. 81 (1984) 5906; J. Noga, R.J. Bartlett, M. Urban, Chem. Phys. Lett. 134 (1987) 146.
[16] J.F. Stanton, Chem. Phys. Lett. 281 (1997) 130.
[17] See for example T.J. Lee, G.E. Scuseria, J. Chem. Phys. 93 (1990) 489.
[18] T.H. Dunning, K.A. Peterson, D.E. Woon, in: P.v.R. Schleyer (Ed.), Encyclopedia of Computational Chemistry, John Wiley & Sons, New York, 1998.
[19] C. Hättig, W. Klopper, A. Köhn, D.P. Tew, Chem. Rev. 112 (2012) 4.
[20] L.A. Curtiss, P.C. Redfern, K. Raghavachari, J. Chem. Phys. 126 (2010) 084108.
[21] J.M.L. Martin, G. de Oliveira, J. Chem. Phys. 111 (1999) 1843.
[22] N.J. DeYonker, T. Grimes, S. Yockel, A. Dinescu, B. Mintz, T.R. Cundari, A.K. Wilson, J. Chem. Phys. 125 (2006) 104111.
[23] P. Hobza, Acc. Chem. Res. 45 (2012) 663.
[24] J. Rezac, K.E. Riley, P. Hobza, J. Chem. Theory Comput. 7 (2011) 3466.
[25] A. Tajti, P.G. Szalay, A.G. Császár, M. Kállay, J. Gauss, E.F. Valeev, B.A. Flowers, J. Vázquez, J.F. Stanton, J. Chem. Phys. 121 (2004) 11599.
[26] A. Karton, E. Rabinovich, J.M.L. Martin, B. Ruscic, J. Chem. Phys. 125 (2006) 144108.
[27] J.A. Pople, J.S. Binkley, R. Seeger, Int. J. Quantum Chem. 10 (1976) 1.
[28] J.S. Binkley, J.A. Pople, Int. J. Quantum Chem. 9 (1975) 229.
[29] J.A. Pople, R. Seeger, R. Krishnan, Int. J. Quantum Chem. Symp. 11 (1977) 149.
[30] R. Krishnan, J.A. Pople, Int. J. Quantum Chem. 14 (1978) 91.
[31] M.J. Frisch, R. Krishnan, J.A. Pople, Chem. Phys. Lett. 75 (1980) 66.
[32] K. Raghavachari, J.A. Pople, E.S. Replogle, M. Head-Gordon, J. Phys. Chem. 94 (1990) 5579.
[33] J.A. Pople, R. Krishnan, H.B. Schlegel, J.S. Binkley, Int. J. Quantum Chem. 14 (1978) 545.
[34] J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, L.A. Curtiss, J. Chem. Phys. 90 (1989) 5622.
[35] L.A. Curtiss, C. Jones, G.W. Trucks, K. Raghavachari, J.A. Pople, J. Chem. Phys. 93 (1990) 2537.
[36] L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, J. Chem. Phys. 94 (1991) 7221.
[37] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, J. Chem. Phys. 106 (1997) 1063.
[38] L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov, J.A. Pople, J. Chem. Phys. 109 (1998) 7764.
[39] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, J. Chem. Phys. 112 (2000) 1125.
[40] L.A. Curtiss, P.C. Redfern, K. Raghavachari, J.A. Pople, J. Chem. Phys. 114 (2001) 108.