Bartlett R J & Purvis G D. Many-body perturbation theory, coupled-pair many-electron theory, and the importance of quadruple excitations for the correlation problem. *Int. J. Quantum Chem.* 14:561-81, 1978.
[Battelle Columbus Laboratories, Columbus, OH]

Many-body perturbation theory, coupled-cluster theory, and configuration interaction are investigated, with particular emphasis on the importance of quadruple excitations in theories of electron correlation. The different methods are used to obtain correlation-energy contributions for a series of molecules: CO_2, HCN, N_2, CO, BH_3, and NH_3. [The *SCI®* indicates that this paper has been cited in over 240 publications.]

Accurate Coupled-Cluster Solutions of the Molecular Schrödinger Equation

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This paper derives from the proceedings of an invited talk I presented at the American Conference on Theoretical Chemistry (ACTC) in 1978. Besides being timely scientifically, the paper's creation offers some amusing insight into how science is done.

Quantum chemistry approxim: ly solv "he Schrödinger equation. To be *predictive* "electron correlation" must be included. In the 1950s two developments occurred that would have important ramifications for the problem of correlation. The first was the work of K.A. Brueckner and J. Goldstone, who recognized that certain terms in Rayleigh-Schrödinger perturbation theory that had the wrong behavior on the number of electrons in a system would cancel from the exact energy and wavefunction. Without this cancellation no meaningful answers could be obtained for extended systems, and poorer results would be obtained for small molecules. These unphysical terms came to be called "unlinked" diagrams because of the use of field-theory methods in establishing the fact that the correct energy and wavefunction are obtained exclusively from linked diagrams. The approach based upon the linked-diagram theorem was termed *(many-body)* perturbation theory because it was suitable for many-electron systems. We presented some of the initial molecular applications in 1974. (See reference 1 for a review.)

Another aspect of the same physics is that the linked-diagram wavefunction could be written in terms of an exponential cluster-type operator. This was recognized by Hubbard, F. Coester, and H. Kümmel and eventually became the basis for cou-

pled-cluster (CC) theory. In applications to correlation this offered an alternative to finite-order many-body perturbation theory (MBPT): choosing instead to evaluate selected cluster contributions to all orders of perturbation theory. Initial equations for the CC double excitation (CCD) approximation were presented by J. Čížek,[2] under the term *coupled-pair many-electron theory.*

My paper with G.D. Purvis offers three elements: (1) Along with the adjacent paper by J.A. Pople *et al.*,[3] it reports the first general *ab initio* applications of the CCD method for a variety of small molecules. (2) It reports on the often important effects of quadruple excitations in molecular calculations for both CCD and MBPT. Such information had not been generally obtainable from the configuration interaction (CI) method because of different computational limitations. (3) It emphasizes the importance of correct scaling with molecular size in quantum chemistry (i.e., size-extensivity), showing that CC/MBPT methods eliminate the important unlinked-diagram error remaining in CI methods. The paper's popularity derives from the crystallization of these three developments in 1978, combined with the later, extensive application of CC/MBPT approaches as an alternative to the older CI method. I understand this paper is the eighth most-cited paper from the *International Journal of Quantum Chemistry.*

To get results prior to the ACTC, we worked feverishly at debugging our code. As often happens just when you are about to get long-sought results, fate intervened ghtning struck the Battelle laboratory and decommissioned the computer! After another two days recovering, we ran calculations day and night, with Purvis staying behind an extra day to obtain the final results.

Considering the complexity of the CC/MBPT equations and programs, internal checks may not reveal all errors in codes; but, when doing new things, you seldom have an independent check. In this instance, we knew that Pople's group was writing programs for the same purpose. Pople was also scheduled to speak at the ACTC. Armed with results for the same trial molecule, we met with Pople the Sunday before the ACTC began and compared numbers. To our mutual relief, the independently computed values agreed, enabling us to present our lectures as planned!

Since 1978 we have extended CC methods to include single excitations (CCSD)[4] and triple excitations (CCSDT),[5] demonstrating highly accurate results for a variety of molecular properties. Attesting to accuracy versus efficiency, in the last two years CC methods have become the method of choice for other computational-chemistry groups.[6] This should guarantee the long-term impact of CC methods in chemistry.

1. Bartlett R J. Many-body perturbation theory and coupled cluster theory for electron correlation in molecules. *Annu. Rev. Phys. Chem.* 32:359-401, 1981. (Cited 290 times.)
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