This paper demonstrated numerically that contributions from quadruply excited configurations make an important energy contribution even for molecules as small as N_2. More importantly, for molecules of moderate size, the energy contribution from these configurations can be estimated by a formula using quantities available from a much simpler configuration-interaction calculation involving only doubly excited configurations. [The *SCI®* indicates that this paper has been cited in over 440 publications.]

Ernest R. Davidson
Department of Chemistry
Indiana University
Bloomington, IN 47405
and
Stephen R. Langhoff
RTC-230-3
NASA Ames Research Center
Moffett Field, CA 94035

March 29, 1988

During the 1960s methods were being developed for treating electron correlation in molecules. Electron correlation, defined as the error in the molecular orbital Hartree-Fock approximation, has a large effect on bond dissociation energies, ionization potentials, electron affinities, excitation energies, and molecular properties. The configuration-interaction (CI) method that included only doubly substituted configurations (SDCI) emerged as the generally accepted method, in part owing to the computational difficulty of including higher than double excitations. During the early 1970s the SDCI method was applied extensively to study the spectroscopy of small molecules.

We were aware, however, of a body of early literature that indicated that the SDCI approach must fail as the number of electrons increased.[1] The problem is that the importance of simultaneous pair excitations increases with the number of electrons. This so-called size-consistency problem meant that the energy of two moles of helium gas is not double the energy of one mole at the SDCI level. The importance of electron correlation (and of higher than double excitations) is also illustrated by the fact that the overlap of the Hartree-Fock wave function with the exact wave function decreases exponentially with the number of atoms in a cluster. Problems with size-consistency were a principal motivating force for the development of diagrammatic many-body perturbation theory and cluster expansion methods.[2]

With this paper we demonstrated that the energy contribution of quadruple excitations could be estimated by the simple equation $\Delta E(1-c_0^2)$, where ΔE is the correlation energy and c_0 is the coefficient of the Hartree-Fock configuration in the SDCI wave function. This energy correction is based (loosely) on the early perturbation theory derivations, where it can be shown that the dominant effect of quadruple excitations is to cancel other "unlinked cluster" terms (simultaneous pair correlation) that otherwise occur in the energy of a doubly excited CI calculation. This cancellation is at the heart of the unlinked clusters theorem. In effect, this so-called quadruples, Davidson, or $+Q$ correction is an approximate correction for lack of size-consistency.

The ease of application, along with its semiquantitative accuracy, led to the widespread use of the $+Q$ correction among quantum chemists. The first publicity for this work came as part of an invited lecture at the First International Congress on Quantum Chemistry held in Menton, France, in 1973, given by the senior author on the occasion of his being named laureate of the International Academy of Molecular Quantum Science.[3] Also, both of the authors spent time at Battelle Memorial Institute with I. Shavitt. Perhaps the earliest use by another research group was the paper by B.J. Rosenberg, W.C. Ermler, and Shavitt, where the $+Q$ correction was shown to give a much-improved calculated geometry for the water molecule.[4]

Subsequently, the basic equation has been extended to be used with multireference wave functions and various "improvements" have been suggested. Recent full CI calculations demonstrate that the $+Q$ correction does indeed account for most of the effect of higher excitations, when the Hartree-Fock configuration provides a good zeroth-order approximation to the wave function. As with many simple ideas, the results are much better than they should be. The surprise is not that the correction occasionally fails, but that it generally works so well. Because of its success, numerous papers have appeared justifying or correcting it.[5,6]

1. **Brueckner K A.** Many-body problem for strongly interacting particles. II. Linked cluster expansion.
   Phys. Rev. 100:36-45, 1955. (Cited 360 times.)
2. **Lefebvre R & Moser C,** eds. Correlation effects in atoms and molecules. (Whole issue.)
   Advan. Chem. Phys. 14, 1969. 545 p.
3. **Davidson E R.** Configuration-interaction description of electron correlation. (Daudel R & Pullman B, eds.) *The world of quantum chemistry.* Dordrecht, Holland: Reidel, 1974. p. 17-30.
4. **Rosenberg B J, Ermler W C & Shavitt I.** Ab initio SCF and CI studies on the ground state surface of the water molecule. II. Potential energy and property surfaces. *J. Chem. Phys.* 65:4072-80, 1976. (Cited 105 times.)
5. **Davidson E R & Silver D W.** Size consistency in the dilute helium gas electronic structure.
   Chem. Phys. Lett. 53:403-6, 1977. (Cited 110 times.)
6. **Siegbahn E M.** Multiple substitution effects in configuration-interaction calculations. *Chem. Phys. Lett.* 55:386-94, 1978. (Cited 40 times.)

/13-6