# On The Importance of Size-Consistency Corrections in Semiempirical MNDOC Calculations

**Dieter Cremer**

*Lehrstuhl für Theoretische Chemie, Universität Köln, Greinstraße 4, D-5000 Köln 41, West Germany*

**Walter Thiel**

*Theoretische Chemie-FB 9, Universität Wuppertal, Gaußstr. 20, D-5600 Wuppertal 1, West Germany*

*Received 4 March 1986; accepted 13 March 1986.*

Energies obtained by configuration interaction calculations including all double excitations with regard to the Hartree-Fock reference determinant can empirically be corrected to size consistency using either the Langhoff-Davidson (LD) formula or a formula suggested by Pople, Seeger, and Krishnan (PSK). Semiempirical MNDOC calculations suggest that for molecular systems with a large number of electrons and important correlation effects the PSK correction is superior to the LD correction.

Often the ground-state correlation energy of molecules is assessed by the method of configuration interaction (CI) utilizing the Hartree-Fock (HF) determinant as reference and considering all double excitations (D).[1] The DCI approach successfully has been applied in many cases both at the nonempirical and semiempirical level. Nevertheless, it has been recognized early that HF DCI is not size consistent, i.e., the computed energy calculated for an assembly of noninteracting molecules A, B, ... is not equal to the sum of the energies obtained for the isolated molecules A, B, ... This is due to the fact that energy contributions from unlinked clusters do not cancel in limited CI expansions.[2–4]

In order to correct for the size consistency error of DCI calculations, at least in an approximate way, an empirical correction formula has been suggested by Langhoff and Davidson (LD).[5,6]

$$\Delta E \approx \Delta E(\mathrm{DCI}) + (1 - C_0^2) \cdot \Delta E(\mathrm{DCI}) \qquad (1)$$

where $\Delta E$ is the total correlation energy, $\Delta E$(DCI) is the part of the correlation energy due to double excitations, and $C_0$ is the coefficient of the HF determinant in the normalized DCI wave function. The second term of eq. (1) may be considered as a reasonable estimate of the quadruple excitation contribution to the CI correlation energy.[5–7]

Pople, Seeger, and Krishnan (PSK)[8] have pointed out that formula 1 is not appropriate for a two-electron system (where $\Delta E = \Delta E(\mathrm{DCI})$) as well as for large molecules where higher excitations become important. Therefore, these authors derived the alternative formula:

$$\Delta E \approx \frac{[n^2 + 2n \tan^2(2\theta)]^{1/2} - n}{2[\sec(2\theta) - 1]} \cdot \Delta E(\mathrm{DCI}) \qquad (2)$$

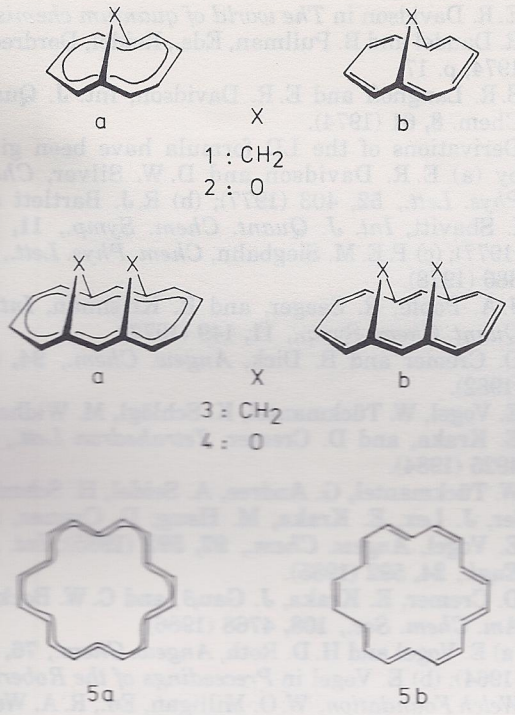
where $n$ is the number of electrons and $\cos\theta = C_0$. Formula (2) is correct for $n = 2$ and contains formula (1) as a special case.[8]

We have recently been engaged in the calculation of bridged annulenes containing 10 to $14\pi$ electrons.[9–12] In these systems complete delocalization of $\pi$ electrons is inhibited by nonplanarity of the annulene perimeter and a resultant decrease in $\pi$ orbital overlap. As a consequence, bridged annulenes, even of the Hückel-type, show some bond alternation. Nevertheless, all experimental observations suggest that the $C_{2v}$ symmetrical bond-equalized geometries of bridged [10], and [14]annulenes (Fig. 1, formula **1a–4a**) are more stable than the bond alternate $C_s$ symmetrical forms **1b–4b**.[13,14]

HF calculations with minimal and DZ basis sets tend to overestimate bond alternation both in $C_{2v}$ and $C_s$ symmetrical forms of

Journal of Computational Chemistry, Vol. 8, No. 1, 48–50 (1987)

CCC 0192-8651/87/010048-03$04.00




bridged annulenes. In addition, they falsely predict the latter to be more stable, an artifact which can only be corrected when correlation effects are considered.[9,15,16] The calculational costs, however, become excessive at this level of theory.

In this situation a reasonable alternative for a quantum chemical description of bridged annulenes is provided by MNDO methods.[17,18] With MNDO itself $\pi$ electron delocalization and bond equalization is better described than at the nonempirical level, although the major drawback of the HF approach is also reflected by MNDO results: The $C_2$ symmetrical forms **1b–4b** are still more stable than the $C_{2v}$ symmetrical forms **1a–4a**.[22]

A rather simple improvement of calculated relative $\Delta H_f^\circ$ values, however, can be achieved by the correlation corrected version of MNDO (MNDOC).[18] MNDOC has been reparametrized for a treatment of electron correlation by second-order perturbation theory using a Brillouin-Wigner (BW) expansion in connection with Epstein-Nesbet (EN) energy denominators.[18] The MNDOC/BWEN approach can be regarded as an approximate CI treatment, equivalent to the diagonalization of a CI matrix with nonzero elements only on the diagonal and in the first row (column). Accordingly, MNDOC/BWEN reproduces MNDOC/D CI correlation energies satisfactorily.[18]

When incorporating size consistency corrections for the set of 61 test molecules with $n \leq 26$ in the original MNDOC study,[18] it was found that these corrections were generally small (about 6% of $\Delta E$(DCI), on the average 1.5 kcal/mol) and that the LD and PSK values were always almost identical (within 0.1 kcal/mol). It is known, however, that the size consistency corrections become more important for molecules with a larger number of electrons, such as compounds **1–4**.

In Table I relative MNDOC enthalpies are given for some selected compounds. In the case of the [10]annulene **2**, the BWEN correlation effects already reverse the relative stability of **a** and **b** forms, while for **1** and the $14\pi$ systems these corrections do not suffice. A further improvement, however, is obtained when size consistency errors are estimated utilizing either formula 1 or 2 (Table I). The PSK corrections are clearly larger than the LD corrections. As a consequence, relative $\Delta H_f^\circ$(MNDOC/BWEN) values corrected

**Table I.** Absolute and relative heats-of-formation (in kcal/mol) of some bridged annulenes.[a]

| Method | **1a** | **1b** | $\Delta\Delta H_f^\circ$ | **2a** | **2b** | $\Delta\Delta H_f^\circ$ | **3a** | **3b** | $\Delta\Delta H_f^\circ$ | **4a** | **4b** | $\Delta\Delta H_f^\circ$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_{2v}$ | $C_s$ | | $C_{2v}$ | $C_s$ | | $C_{2v}$ | $C_s$ | | $C_{2v}$ | $C_s$ | |
| $n$[b] | 54 | 54 | | 54 | 54 | | 78 | 78 | | 78 | 78 | |
| MNDOC/SCF | 170.2 | 163.9 | −6.3 | 143.4 | 139.2 | −4.2 | 255.1 | 240.0 | −15.1 | 200.7 | 185.2 | −15.5 |
| MNDOC/BWEN | 92.5 | 92.1 | −0.4 | 61.3 | 62.5 | 1.2 | 147.1 | 141.3 | −5.8 | 90.5 | 84.7 | −5.8 |
| LD correction[c] | −10.8 | −8.6 | | −11.6 | −9.5 | | −17.8 | −13.6 | | −18.3 | −14.4 | |
| MNDOC/BWEN+LD | 81.7 | 83.4 | 1.7 | 49.7 | 53.0 | 3.3 | 129.3 | 127.7 | −1.6 | 72.2 | 70.8 | −1.4 |
| PSK correction[c] | −14.2 | −10.8 | | −15.3 | −12.1 | | −25.4 | −18.1 | | −27.3 | −19.1 | |
| MNDOC/BWEN+PSK | 78.3 | 81.3 | 3.0 | 46.0 | 50.4 | 4.4 | 121.7 | 123.2 | 1.5 | 63.2 | 65.6 | 2.4 |

[a] For geometries see ref. 12.
[b] $n$ denotes the number of valence electrons.
[c] size consistency correction estimated by the Langhoff-Davidson (LD) or the Pople-Seeger-Krishnan (PSK) formula.

by the PSK formula lead to the correct order of stabilities of all $C_{2v}$ and $C_s$ symmetrical bridged annulenes while LD corrections are too small for larger annulenes and, therefore, cannot provide correct stabilities.

These results led us to reconsider the case of [18]annulene **5**. Previous MNDOC-BWEN calculations with LD corrections[19] yielded almost the same energy for the delocalized $D_{6h}$ (**5a**) form and the localized $D_{3h}$ (**5b**) form ($D_{6h}$ marginally more stable by 1.1 kcal/mol). According to our present findings, however, the PSK correction should be more appropriate for such a large molecule ($n = 90$). With the PSK correction, the delocalized $D_{6h}$ structure is clearly preferred, by 8.4 kcal/mol, in agreement with experimental data.[20]

We *conclude* that MNDOC/BWEN or MNDOC/DCI results can be improved by using the PSK rather than the LD formula to estimate the size consistency error. For molecules with a large number of electrons and important correlation effects, the PSK correction appears to be superior to the LD correction. This is consistent with the fact that the LD formula works best for systems with a smaller number of electrons.[21] Similar conclusions should apply to nonempirical treatments.

## References


1. I. Shavitt in *Modern Theoretical Chemistry,* Vol. 3, H. F. Schaefer, III, Ed., Plenum Press, New York, 1976, p. 189.
2. W. Meyer, *J. Chem. Phys.,* **58,** 1017 (1973).
3. R. J. Bartlett and D. M. Silver, *Int. J. Quant. Chem. Symp.,* **9,** 183 (1975).
4. J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quant. Chem. Symp.,* **10,** 1 (1976).
5. E. R. Davidson in *The world of quantum chemistry,* R. Daudel and B. Pullman, Eds., Reidel, Dordrecht, 1974, p. 17.
6. S. R. Langhoff and E. R. Davidson, Int. J. Quant. Chem. **8,** 61 (1974).
7. Derivations of the LD formula have been given by (a) E. R. Davidson and D. W. Silver, *Chem. Phys. Lett.,* **52,** 403 (1977); (b) R. J. Bartlett and I. Shavitt, *Int. J. Quant. Chem. Symp.,* **11,** 165 (1977); (c) P. E. M. Siegbahn, *Chem. Phys. Lett.,* **55,** 386 (1978).
8. J. A. Pople, R. Seeger, and R. Krishnan, *Int. J. Quant. Chem. Symp.,* **11,** 149 (1977).
9. D. Cremer and B. Dick, *Angew. Chem.,* **94,** 877 (1982).
10. E. Vogel, W. Tückmantel, K. Schlögl, M. Widhalm, E. Kraka, and D. Cremer, *Tetrahedron Lett.,* **25,** 4925 (1984).
11. W. Tückmantel, G. Andree, A. Seidel, H. Schmickler, J. Lex, E. Kraka, M. Haug, D. Cremer, and E. Vogel, *Angew. Chem.,* **97,** 592 (1985); *Int. Ed. Engl.,* **24,** 592 (1985).
12. D. Cremer, E. Kraka, J. Gauβ, and C. W. Bock, *J. Am. Chem. Soc.,* **108,** 4768 (1986).
13. (a) E. Vogel and H. D. Roth, *Angew. Chem.,* **76,** 145 (1964); (b) E. Vogel in *Preceedings of the Robert A. Welch Foundation,* W. O. Milligan, Ed., R. A. Welch Foundation 1968, p. 215; (c) E. Vogel, *Pure Appl. Chem.,* **20,** 237 (1969); (d) E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer, and H. Günther, *Liebigs Ann. Chem.,* **759,** (1972).
14. H. Günther and H. Schmickler, *Pure Appl. Chem.,* **44,** 807 (1975).
15. L. Farnell and L. Radom, *J. Am. Chem. Soc.,* **104,** 7650 (1982).
16. R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.,* **107,** 289 (1985).
17. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.,* **99,** 4899 (1977).
18. W. Thiel, *J. Am. Chem. Soc.,* **103,** 1413 (1981).
19. W. Thiel, *J. Am. Chem. Soc.,* **103,** 1420 (1981).
20. J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta. Crystallogr.,* **19,** 227 (1965).
21. A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry,* Macmillan Publishing Co., New York, 1982, p. 268.
22. M. J. S. Dewar and M. L. McKee, *Pure Appl. Chem.* **52,** 1431 (1980) have suggested to circumvene this problem by employing UMNDO, the UHF version of MNDO.