Theoret. chim. Acta (Berl.) 16, 401—402 (1970)

Relatio

Uses of Pair Energy Techniques in Molecular Calculations: The Ammonia Molecule

C. F. Bender
Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201

Received January 5, 1970

Pair energy techniques are used for geometry determinations and calculation of the barrier height in ammonia. The results, when compared with configuration interaction results, are very encouraging.

There has been a great deal of discussion [1–5], on the usefulness of energies calculated using Nesbet's [6] (or variations) pair energy techniques. Recently it has been suggested [7] that the error in the sum of the pair energies depends on the number of electrons. If this is true, energy differences for isoelectric systems and different molecular geometries may not reflect the error in the sum [8]. Preliminary results for ionization energies in atoms tend to strengthen this idea [9]. It is the purpose of this note to examine the use of pair energy techniques in large scale molecular calculations. In particular, the barrier height and geometry determinations for ammonia are analyzed.

The basis set (approximately a double zeta STO set), SCF energies have been given elsewhere [10, 11]. With the SCF electronic configuration given as

$$\phi_0 = a_1^2 a_2^2 a_3^2 e^4 , \tag{1}$$

the symmetry adapted pairs were selected to be,

$$a_1^2, a_2^2, a_3^2, e^2, a_1 a_2, a_1 a_3, a_2 a_3, a_1 e, a_2 e, a_3 e . \tag{2}$$

This choice of the pairs generally follows the ideas of Viers, *et al.* [3] rather than Nesbet [6]. An e^2 pair includes e_+^2, e_-^2, and $e_- e_+$ terms and $a_i e$ includes both $a_i e_+$ and $a_i e_-$. In all calculations the canonical SCF (occupied and unoccupied) orbitals were used.

Table 1 gives the total energies for the pyramidal ($\sphericalangle \mathrm{HNH} = 106.72°$ and $R_{\mathrm{NH}} = 1.911$ bohr) and the planar ($R_{\mathrm{NH}} = 1.911$ bohr) geometries. SCF, CI (including all singly and doubly excited configurations) and two pair energy sums are reported. One of the sums corresponds to neglecting all excitations from the inner shell (a_1) orbitals. The calculated barriers for all four cases are also given. The barriers calculated using the sum of the pair energies differ somewhat from the CI result, but not to the extent that the total energies differ. Geometry predictions have been investigated in the planar case where R_{NH} is unknown experimentally. A three point grid ($R_{\mathrm{NH}} = 1.811, 1.861, 1.911$ bohr) was used in the geometry determination. Table 2 gives the interpolated R_{NH} distance and the

Table 1. *Total energies and barriers*[a]

	Pyramidal	Planar	Barrier[c]
SCF	−56.19525	−56.19142	0.00383
CI[b]	−56.35637	−56.34807	0.00830
$SCF+\sum_{i>j}\varepsilon_{ij}$	−56.37302	−56.36330	0.00972
$SCF+\sum_{i>j\neq a_1}\varepsilon_{ij}$	−56.35563	−56.34579	0.00984

[a] All energies reported in hartrees.

[b] SCF + all single and double replacement configurations.

[c] Experimental value 0.0092 .

Table 2. *Geometry determination*

	Interpolated R_{NH}	Interpolated energy minimum
SCF	1.868	−56.19295
CI	1.879	−56.34892
$SCF+\sum_{i>j}\varepsilon_{ij}$	1.883	−56.36393
$SCF+\sum_{i>j\neq a_1}\varepsilon_{ij}$	1.884	−56.34640

corresponding energy for the SCF, CI, and two pair energy calculations. Again the results are very encouraging.

The calculations presented here indicate that *pair energy techniques may be useful in large scale molecular calculations.* Within the accuracy of the basis, the effect due to excitations from the inner shell may be neglected, thus reducing (from 10 to 6 in NH_3) the number of pair calculations. Unfortunately only further studies on a wide range of molecular systems will determine the reliability of such methods. The dependence of energy differences on unitary rotations is currently under investigation.

The author wishes to express his thanks to Dr. A. Pipano whose CI programs made this study possible and to Dr. R. R. Gilman and Professor I. Shavitt for many helpful and stimulating discussions.

References

1. Bender, C. F., Davidson, E. R.: J. chem. Physics **49**, 465 (1968).
2. — — Chem. Physics Letters **3**, 33 (1969).
3. Viers, J. W., Harris, F. E., Schaefer III, H. F.: Physic Rev., to be published.
4. Nesbet, R. K., Barr, T. L., Davidson, E. R.: Chem. Physics Letters **4**, 203 (1969).
5. Barr, T. L., Davidson, E. R.: Physic. Rev., to be published.
6. Nesbet, R. K.: Physic. Rev. **155**, 51, 56 (1967), **175**, 2 (1968).
7. Bender, C. F., Davidson, E. R.: Physic. Rev. **183**, 23 (1969).
8. Krauss, M.: private communication.
9. Weiss, A. W.: private communication.
10. Pipano, A., Gilman, R. R., Bender, C. F., Shavitt, I.: Chem. Physics Letters, to be published.
11. — —, Shavitt, I.: to be published.

Dr. Charles F. Bender
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201, USA