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D. GraveronDemilly

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$$E = \frac{3}{7}(V_{Ne} + 2V_{NN}) \quad (2)$$

where V_{Ne} and V_{NN} denote respectively the total nuclear-electron attraction energy and nuclear-nuclear repulsion energy. Referring to Standard SCF Calculations,³ which have employed basis sets of generally double-zeta quality, Politzer² has shown that the right-hand side of Eq. (2) overestimates the total SCF energy of molecules by $\sim 1\%$. Based on this observation, Ruedenberg¹ has argued that the relation

$$E = 1.55 \sum_k \nu_k \epsilon_k \quad (3)$$

should be a somewhat closer approximation.

It is well known that the virial relation $V/E=2$ is satisfied at the calculated equilibrium geometry of a molecule by a total wavefunction built up from exact HF orbitals or SCF orbitals, where the exponents of the constituent AO's have been rigorously optimized. The Politzer relation (2) is also expected to be dependent upon the basis set. Thus, defining $\alpha = E/(V_{Ne} + 2V_{NN})$ and $\beta = V/E$, where α and β depend upon the basis set, one can easily obtain the more general relation

$$E = \frac{\alpha}{\alpha + \alpha\beta - 1} \sum_k \nu_k \epsilon_k = \gamma \sum_k \nu_k \epsilon_k \quad (4)$$

It is readily seen that $\gamma = 1.5$, when $\alpha = \frac{3}{7}$ and $\beta = 2$. Equation (4) also shows that γ varies more sharply with α than with β .

We have computed γ values for about 100 molecules from their SCF calculation as available in the literature.⁴ In these calculations, basis sets ranging from minimal to near HF quality have been employed. It is found that γ varies from 1.28 to 1.75, which is in sharp contradiction to Eq. (1) or (3). In majority of the cases $\gamma > 1.6$ and it is less than 1.5 for about 20 molecules. Since β is very close to 2 in most of these calculations, it is implied that α can deviate by as much as $\pm 5\%$ from the Politzer's value of $\frac{3}{7}$. But an error of 5% in α introduces an error of about 15% in γ . We are thus led to the conclusion that the identity of Eq. (1) or (3) is too approximate to be of any general practical application.

¹K. Ruedenberg, J. Chem. Phys. **66**, 375 (1977).

²P. Politzer, J. Chem. Phys. **64**, 4239 (1976).

³L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties* (Wiley-Interscience, New York, 1972).

⁴Data taken mostly from the papers published in J. Chem. Phys. during last ten years.

ERRATA

Erratum: Conformational maps of some saturated six and seven membered rings [J. Chem. Phys. **66**, 2874 (1977)]

D. Graveron-Demilly

Laboratoire de Spectroscopie et de Luminescence, Université Claude Bernard Lyon I, 43, Boulevard du 11 Novembre 1918, 69621 Villeurbanne, France

Professor H. L. Strauss has brought to my attention an error which affects the θ characteristic value for both chair and twist-chair conformations of cycloheptane. Our previously reported results correspond to an implicit value $C=1$.¹ In fact, the angle $\theta \approx 71^\circ$ characterizes the chair conformation for $C=1.7$, and for $C=1$ the corresponding value is about 59° . The revised results are displayed in Table I.

The twist-chair conformation is found to be the lowest energy form; this result is in agreement with Ref. 2. It should be noted that for $75^\circ < \theta < 90^\circ$ the energies of the twist-chair and the chair conformations differ by less than 0.05 Kcal.

The above correction does not affect our preceding conclusions.

TABLE I. Conformational energies (in kcal/mole).

	θ	ΔE
Boat	2.5	12.02
Twist-boat	4.5	11.66
Chair	71	2.20
Twist-chair	71	2.07
Chair	59.15	0.99
Twist-chair	54.15	0.00

We are very grateful to Drs. J. L. Offenbach and H. L. Strauss for pointing out this error.

¹ $Z_j = \gamma [C \cos(4\pi j/7 + \Phi_2) \cos \theta + \cos(6\pi j/7 + \Phi_3) \sin \theta]$.

²D. F. Bocian, H. M. Pickett, T. C. Rounds, and H. L. Strauss, J. Am. Chem. Soc. **97**, 687 (1975).