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Relationes

Determination of Approximate Bond Dissociation Energies by a Semi-Empirical MO Technique

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It is suggested that the Extended Hückel Method by Hoffmann may be used for the determination of approximate bond dissociation energies.

Several years ago, in a classic paper dealing with hydrocarbon conformational problems, Hoffmann [1] introduced what is generally known today as the Extended Hückel method. The purpose of the present note is to suggest that with slight modification, the latter may be used for the determination of approximate bond dissociation energies D.

The technique, as extended by us, requires *only* the adjustment of the proportionality constant(s) used in the semi-empirical estimation of the resonance integrals $\hat{H}_{ij}$ such that the minimum of the calculated total energy $E_T(r)$ coincides with the experimentally obtained average internuclear distance[1]. That is, for a specific F_σ and F_π combination, when r (min. E_T) is approximately[2] equal to r_0, we then expect, for N equivalent bonds,

$$N \cdot D \approx E_T(r_0) - E_T(\infty) .$$

To illustrate our proposed technique, we have considered the bond dissociation of the σ-bonded tetrahedral molecules CH_4 and SiH_4, as well as their isoelectronic NH_4^+ and PH_4^+ ions. Furthermore, we have carried our computations within the following framework:

(i) In all cases we have used SCF wavefunctions as given by Clementi [3].

(ii) In all cases we have assumed that the ns and np orbitals ($ns^2 np^n$ configuration) of the central ions were primarily involved in the bonding of these molecules and ions.

(iii) In all cases we have used the calculated atomic orbital energies given by Clementi [3] as the value of the coulomb integrals $\hat{H}_{ii}$.

(iv) In all cases we have used the reciprocal mean [4] to compute the exchange integrals $\hat{H}_{ij}$.

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[1] The applicability of the proposed technique, naturally, depends on the availability of a minimum total energy. It is perhaps instructive to mention that the best SCF-LCAO-MO calculation does not recognize the existence of F_2 [2]!

[2] To the tenth of an Ångstrom.

Table. *Computed and observed molecular parameters*

	CH_4	SiH_4	NH_4^+	PH_4^+
F_σ	1.75	1.90	1.60	1.58
r_0(obs.[a])	1.093 Å	1.480	1.008	1.417
r_0(used)	1.1	1.5	1.0	1.4
D(calc.)	4.2 eV	3.6	2.6	2.0
D(exp.[b])	4.4	3.3	?	?
$(\partial^2 E_T/\partial r^2)_0$	5.04 mdyn/Å	2.84	5.00	3.2
f_R(exp.[c])	5.04	2.84	5.46	3.15

[a] From Ref. [5].
[b] From Ref. [6].
[c] S.V.F. force constants computed from Ref. [7].

The Table gives the experimental as well as the calculated values of the pertinent molecular parameters. Fig. 1, on the other hand, gives the one-electron molecular orbital energies of SiH_4 as a function of the Si–H distance, while Fig. 2 displays the total energy of SiH_4 as a function of the internuclear distance. An examination of the table, indicates that in the known cases the calculated values are very close to the experimentally obtained values, while for the unknown cases they seem to be quite reasonable.

Our confidence in the proposed technique is further enhanced when we consider the following:

(i) The force constants, in the harmonic approximation, agree remarkably well with those obtained from the vibrational spectra.

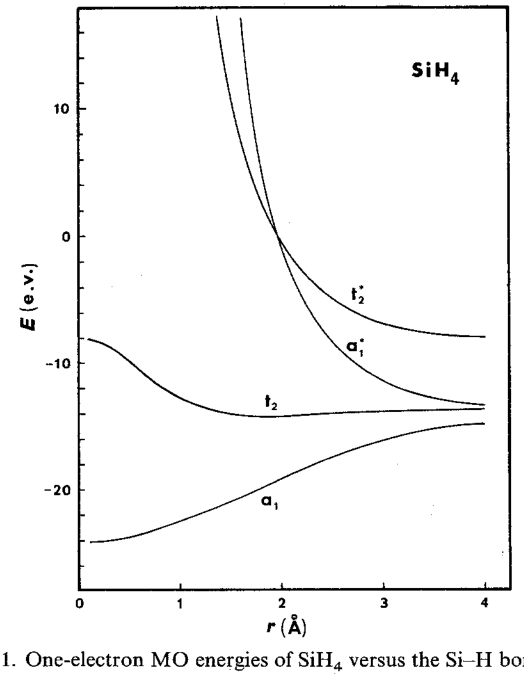

Fig. 1. One-electron MO energies of SiH_4 versus the Si–H bond distance r

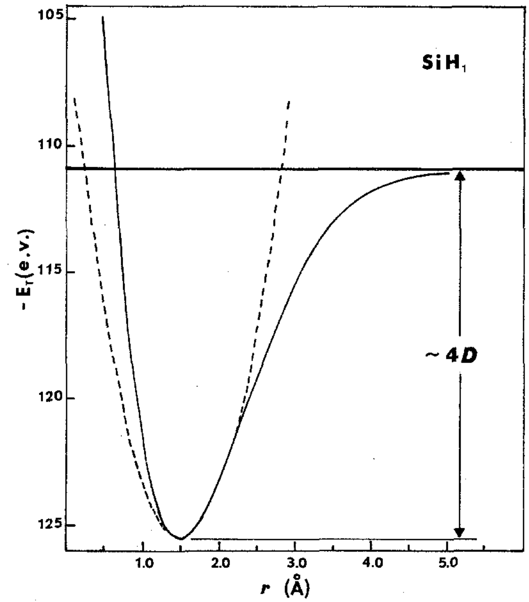

Fig. 2. $E_T(r)$ of SiH_4 plotted versus r (Solid line). Broken line presents the harmonic oscillator approximation

(ii) The ratio of the calculated bond dissociation energies of the ions $D(NH_4^+)/D(PH_4^+)$ is 1.3, which compares favorably with the ratio of 1.2 of the thermochemical bond energies of the parent molecules $E(NH_3)/E(PH_3)$.

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References

1. Hoffmann, R.: J. chem. Physics **39**, 1397 (1963).
2. Wahl, A. C.: J. chem. Physics **41**, 2600 (1964).
3. Clementi, E.: IBM J. Res. Develop. **9**, 2 (1965).
4. Yeranos, W. A.: J. chem. Physics **44**, 2207 (1966).
5. Tables of interatomic distances and configurations in molecules and ions, Special Publication No 11, The Chemical Society, London 1958.
6. Cottrell, T. L.: The strengths of chemical bonds. London: Academic Press 1958.
7. Pistorius, C. W. F. T.: J. chem. Physics **27**, 965 (1957).

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