

# The Use of the Modified Extended Hückel Method in Molecular Dynamics

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Our previously proposed modification of Hoffmann's extended Hückel method is discussed, and its use in the determination of the dissociation energies of  $H_3M-H$  type molecules where the  $H_3M$  moiety is taken as a unit examined. The proposed technique is also used to study the angular dependence of the total potential energy of the previously studied molecules, as a consequence of which it is suggested that the proportionality constants (in this case the  $F_o$ 's) are atom-atom parameters, transferable from molecule to molecule. The latter concept is used in the theoretical determination of the geometries and energetics of  $CH_3$ ,  $SiH_3$ ,  $NH_3$ ,  $PH_3$ , as well as some of their ionic forms. Finally, as a result of our calculations, we suggest that  $CH_3^-$  is planar with a much flatter potential minimum than  $CH_3$ .

## Introduction

Several years ago, in a classic paper dealing with hydrocarbon conformational problems, HOFFMANN<sup>1</sup> introduced what is presently known as the "extended Hückel" method. Although lacking a sound theoretical basis<sup>2</sup>, the paper showed that the Hückel method without the assumption of zero differential overlap could, with one simple parametrization, be used to calculate the basic properties of inorganic structures as well as organic systems, be they aliphatic or aromatic. It seemed, moreover, to equate the sum of the one-electron energies to the true molecular energy<sup>3</sup>. So much so that in the case of methane, for instance, the distance at which the former reached a minimum was considered as the attainment of the equilibrium internuclear distance, and its bond stretching force constant was calculated from the curve near its minimum.

It is important to note, however, that this rough parallelism between the molecular energy and the sum of one-electron energies was not a new idea. Slater had previously pointed it out in his discussion of homonuclear diatomic molecules<sup>4</sup>. It should, nonetheless, be stressed that Slater was actually talking about the sum of one-electron energies obtained from a Hartree-Fock Hamiltonian and *not* from an "effective" Hamiltonian as Hoffmann was.

In a subsequent paper<sup>5</sup> this author extended Hoffmann's formalism and suggested that, given a reformulation of its basic procedural techniques, the method could also be used to obtain, again to a first degree of approximation, the bond dissociation energies of a molecule from its *calculated* atomization energy.

It should be remembered that, in any one-electron model, a typical secular determinantal equation is given by

$$|\hat{h}_{ij} - \epsilon S_{ij}| = 0,$$

from which the spectrum of orbital energies  $\epsilon_k$  can be found if the overlap integrals  $S_{ij} (\equiv \langle \chi_i | \chi_j \rangle)$  as well as the Hamiltonian matrix elements  $\hat{h}_{ij} (\equiv \langle \chi_i | \hat{h} | \chi_j \rangle)$  are known. The  $\chi$ 's in  $S_{ij}$  and  $\hat{h}_{ij}$  are the orbitals believed to be participating in bond formation, while  $\hat{h}$  is an "effective" one-electron Hamiltonian whose explicit form cannot be written down.

In the specific case of Hoffmann's extended Hückel method the overlaps are calculated from Slater orbitals<sup>4</sup>, and the Hamiltonian matrix elements are obtained according to the following recipe. When  $i = j$ , Hoffmann insists that  $\hat{h}_{ii}$  be identified as the valence state ionization potential of  $\chi_i$ , and when  $i \neq j$ , he suggests that  $\hat{h}_{ij}$  be proportional to

<sup>1</sup> R. HOFFMANN, J. Chem. Phys. **39**, 1397 [1963].

<sup>2</sup> Ibid, p. 1400

<sup>3</sup> Here, and elsewhere, we use Hoffman's parlance (see the caption of Fig. 1 in Ref.<sup>1</sup>). We use the "sum of one-electron energies", "calculated total electronic energy", "energy sum" and "total energy" interchangeably to mean the sum of the one-electron M.O. energies multiplied by their respective electron occupancies.

<sup>4</sup> J. C. SLATER, "Quantum Theory of Molecules and Solids", McGraw-Hill Book Company, Inc., New York 1963, Vol. I, p. 108.

<sup>5</sup> W. A. YERANOS, Theor. Chem. Acta, **13**, 346 [1969].



$S_{ij}$ , such that

$$\hat{h}_{ij} = K \left( \frac{\hat{h}_{ii} + \hat{h}_{jj}}{2} \right) S_{ij},$$

where  $K$  is a *molecular* constant to be chosen in such a way as to give the best results for the "total energy".

In our preliminary note<sup>5</sup>, we suggested, in contradistinction to the above procedural technique, that  $K$  be considered a *bond* constant much in the same way that  $F_\sigma$  and  $F_\pi$  were considered in the Wolfsberg-Helmholz formalism which is extensively used in the study of the optical transitions of inorganic complexes<sup>6</sup>. The distinction being, however, that the specific values of  $F_\sigma$  and  $F_\pi$  were to be found by adjusting them so as to make the minimum of the calculated total electronic energy coincident with the experimentally obtained average internuclear distances. Furthermore, having in mind the possible future use of the technique in molecules containing atoms beyond the second row of the periodic table, we insisted that the overlaps, which indeed are the only genuine quantum mechanical entities, be computed by the use of self-consistent field functions<sup>7</sup>. A similar anticipation prompted us, moreover, to "systematize" our procedure of determining the Hamiltonian matrix elements by using Clementi's calculated orbital energies<sup>7</sup> for the  $\hat{h}_{ii}$  rather than be involved in the polemics of what constitutes a valence state in an atom and what should be the value of its ionization potential. The off-diagonal elements  $\hat{h}_{ij}$ , on the other hand, were to be computed by the use of the reciprocal mean<sup>8</sup>

$$\hat{h}_{ij} = F_{\sigma,\pi} \left( \frac{2\hat{h}_{ii}\hat{h}_{jj}}{\hat{h}_{ii} + \hat{h}_{jj}} \right) S_{ij}.$$

|          | Hoffmann  | This Work  |
|----------|---|--|
| $\chi_i$ | Slater Orbitals   | Clementi's S.C.F.  |
| $h_{ii}$ | Valence State I.P.  | Clementi's Calc. Orbit. Energies   |
| $h_{ij}$ | $K \left( \frac{\hat{h}_{ii} + \hat{h}_{jj}}{2} \right) S_{ij}$               | $F_{\sigma,\pi} \left( \frac{2\hat{h}_{ii}\hat{h}_{jj}}{\hat{h}_{ii} + \hat{h}_{jj}} \right) S_{ij}$ |
| $K$      | A <i>Molecular</i> Constant<br>$K(\text{CH}) = 1.75$<br>$K(\text{HH}) = 1.75$ | A <i>Bond</i> Constant<br>$F_\sigma(\text{CH}) = 1.75$<br>$F_\sigma(\text{HH}) = 2.00$               |

Table I. Comparison of Hoffmann's and our Procedural Techniques.

Table I lists the differences between the two approaches, while Fig. 1 displays the "total energy" curve of  $\text{CH}_4$  calculated in our scheme. It is extremely important to stress that it was the Morse-

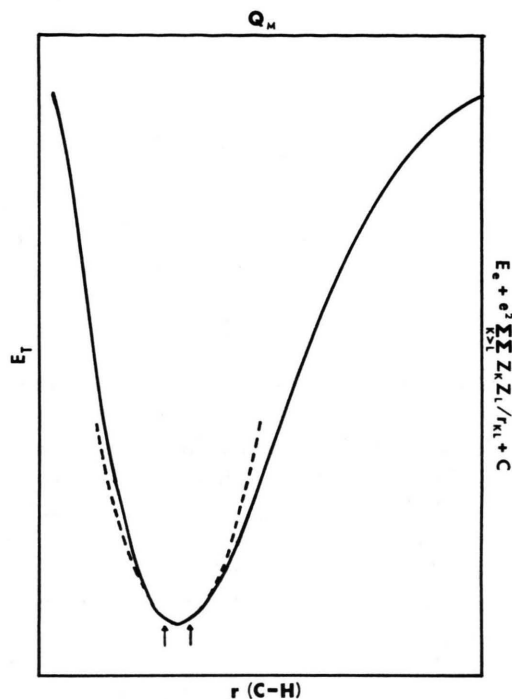


Fig. 1. Equivalence of the Total Potential Energy and the Extended Hückel Total Energy.  $Q_M$  is the "Breathing" Normal Mode.

like behavior of Hoffmann's so called "total energy" of methane as a function of the C—H distance which prompted us to modify his scheme and suggest that the dissociation energy  $D$  of a molecule of  $N$  equivalent bonds be estimated from the *calculated* atomization energy  $Q_a$ . That is

$$D \approx Q_a/N = [E_T(r_e) - E_T(\infty)]/N.$$

We certainly agree that this is not a conventional method of determining bond dissociation energies. The method may seem specially unconventional, and rightly, so when one considers the fact that in all L.C.A.O.-M.O. calculations, the wave functions involved in bonding do not have the correct behavior at infinity. Nevertheless, we agreed to give it a try and were indeed gratified by our results.

Another point which may seem questionable from the strict thermodynamic point of view is our ap-

<sup>6</sup> C. J. BALLHAUSEN and H. B. GRAY, "Molecular Orbital Theory", W. A. Benjamin, Inc., New York 1965.

<sup>7</sup> E. CLEMENTI, IBM J. Res. Develop. **9**, 2 [1965].

<sup>8</sup> W. A. YERANOS, J. Chem. Phys. **44**, 2207 [1966].

proximation of the bond dissociation energy with the "average" bond energy, or what is generally known as the bond energy term. It should be remembered that the "average" bond energy was defined by SZWARC and EVANS<sup>9</sup> and is given by the integral<sup>10</sup>

$$\bar{q}_{ak} = \text{"average" bond energy} = \int_L \frac{\partial E}{\partial r_k} \cdot dr_k$$

where  $L$  denotes the integration path of stretching all the bonds from their original equilibrium values to infinity *without* changing the original shape of the molecule. Needless to say that this integration path is an unnatural one, corresponding to a purely imaginary process. Actually, the physically observable path, henceforth denoted by  $P$ , is the one in which the  $k$ th bond breaks through the infinite elongation of the distance  $r_k$  while the system adjusts itself to the configuration of minimum energy throughout this change. Szwarc and Evans define, mathematically, this process of dissociation by the integral

$D_k$  = dissociation energy of the  $k$ th bond

$$= \int_P \frac{\partial E}{\partial r_k} \cdot dr_k + \int_P A dr_k$$

where the first term on the right-hand side represents the energy due to the breaking of the  $k$ th bond, while the second represents the energy due to the simultaneous changes in the configuration of the rest of the molecule or the "reorganization energy" as LONG and NORRISH<sup>11</sup> have termed it.

It is obvious, then, that any formal mathematical treatment of the above definitions would require a knowledge of the function  $E$  which depends on the nature of the molecular field force. On the other hand, if the force field is taken to be the simple valence force field, then the dissociation energy is identically equal to the "average" bond energy. It is indeed *precisely* within this context that we had, in our preliminary note, proposed the modified use of the extended Hückel method in the determination

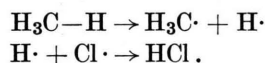
of approximate dissociation energies of the M-H bonds in the considered  $MH_4$  molecules (all of  $T_d$  symmetry). It should be noted that we did not and do not claim that the molecular force field in these molecules is actually a simple valence force one, but what we do stress is that the closeness of our force constants, obtained from the minima of the calculated potential curves, to the simple valence force field constants, obtained from the totally symmetric Raman-active stretching frequencies, seemed to justify our approximation of the "average" bond energies with the dissociation energies.

The purpose of the present investigation is to extend our previous study by examining the applicability of our proposed technique in the "diatomic" approximation of polyatomic molecules, as well as in the determination of the geometries and energetics of the molecules under consideration and some of their ionic and neutral radicals. In particular, it was interesting to see how the technique performed in the estimation of the potential barrier, if any, of  $CH_3^-$  about which there seems to be a great deal of controversy<sup>12,13</sup>.

### The "Diatomic" Approximation

A classical example of the use of this approximation can be found in the kinetic study of the methane-chlorine atom reaction.

It is generally accepted that the reaction proceeds via the dissociation of methane followed by the reaction of the chlorine atom with a hydrogen atom. i. e.,



To simplify matters, moreover, and indeed keep the study within the absolute rate theory<sup>14</sup> tractable, it is also suggested<sup>15</sup> that the  $H_3C-H$  molecule be considered as a diatomic molecule in which the "frozen" methyl radical is taken as one of the "atoms". Naturally, this is an approximation, but,

<sup>9</sup> M. SZWARC and M. G. EVANS, J. Chem. Phys. **18**, 618 [1950].

<sup>10</sup> The average bond energy term  $\bar{q}_{ak}$  has the following properties:

(i)  $\sum_k \bar{q}_{ak} = Q_a$ ;

(ii)  $\bar{q}_{ak} = \bar{q}_{ai}$  for any bond  $k$  and  $i$  which are indistinguishable in the molecule;

(iii) For a molecule containing  $N$  indistinguishable bonds  $\bar{q}_a = Q_a/N$ .

<sup>11</sup> L. H. LONG and R. G. W. NORRISH, Proc. Roy. Soc. London **A187**, 337 [1946].

<sup>12</sup> R. E. KARI and I. G. CSIZMADIA, J. Chem. Phys. **46**, 4585 [1967] and all references listed therein.

<sup>13</sup> R. E. KARI and I. G. CSIZMADIA, J. Chem. Phys. **50**, 1443 [1969].

<sup>14</sup> I. AMDUR and G. G. HAMMES, Chemical Kinetics, McGraw-Hill Book Co., New York 1966.

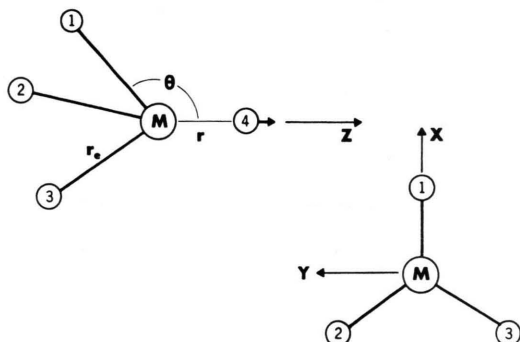
<sup>15</sup> K. B. WIBERG, Physical Organic Chemistry, John Wiley and Sons, Inc., New York 1964.

| Reps  | Orbitals on M | Hydrogen Symmetry Orbitals  |
|-------|---------------|---|
| $a_1$ | $ns, np_z$    | $\sigma_4, \Sigma(a_1) = 3^{-1/2}(\sigma_1 + \sigma_2 + \sigma_3)/(1 + 2\langle\sigma_1 \sigma_2\rangle)^{1/2}$ |
| $e$   | $np_x$        | $\Sigma^a(e) = 6^{-1/2}(2\sigma_1 - \sigma_2 - \sigma_3)/(1 - \langle\sigma_1 \sigma_2\rangle)^{1/2}$           |
|       | $np_y$        | $\Sigma^b(e) = 2^{-1/2}(\sigma_2 - \sigma_3)/(1 - \langle\sigma_2 \sigma_3\rangle)^{1/2}$                       |

Table II. Symmetry orbitals in the  $C_{3v}$  Model.

it is generally conceded that the errors introduced by it are negligible compared to the rest of the approximations that are made.

In the present section we consider this problem within the framework of our proposed technique. Fig. 2 gives the geometric configuration of the entities involved, while Table II displays the orbitals considered in the limiting  $C_{3v}$  symmetry. From Fig. 2, moreover, one notices that there are three apparent  $F_\sigma$ 's to be determined<sup>16</sup>. Confronted with

Fig. 2. Geometric Configuration of  $MH_4$  in the  $C_{3v}$  Model.

this dilemma, we assumed, and rightly so, that the latter were atom-atom parameters and transferable from molecule to molecule. Taking methane as an example, we assumed that  $F_\sigma(CH)$  in both the "mobile"  $C-H_4$  bond and in the "fixed"  $C-H_n$  ( $n = 1, 2, 3$ ) bonds had a single value. In a similar manner the  $F_\sigma(H_iH_j)$ ,  $i \neq j = 1, 2, 3, 4$ , were taken to be the same. Fig. 3 depicts the bond energy term  $E$  as well as the bond dissociation energy  $D$  of  $CH_4$  obtained by

$$(i) \quad E(H_3C-H) = \int_{L}^{\infty} \frac{\partial E}{\partial r_k} \cdot dr_k \quad (\text{Calc. I})$$

<sup>16</sup> These are:

- (i)  $F_\sigma(CH)$
- (ii)  $F_\sigma(H_iH_4) \quad i = 1, 2, 3$
- and
- (iii)  $F_\sigma(H_iH_j) \quad i < j = 1, 2, 3, 4.$

Note that  $F_\sigma(HH)$  was taken equal to 2.00 in all calculations.

and

$$(ii) \quad D(H_3C-H) \approx \int_P^{\infty} \frac{\partial E}{\partial r_k} \cdot dr_k, \quad (\text{Calc. II})$$

while the results for the rest of the molecules considered are given in Table IV.

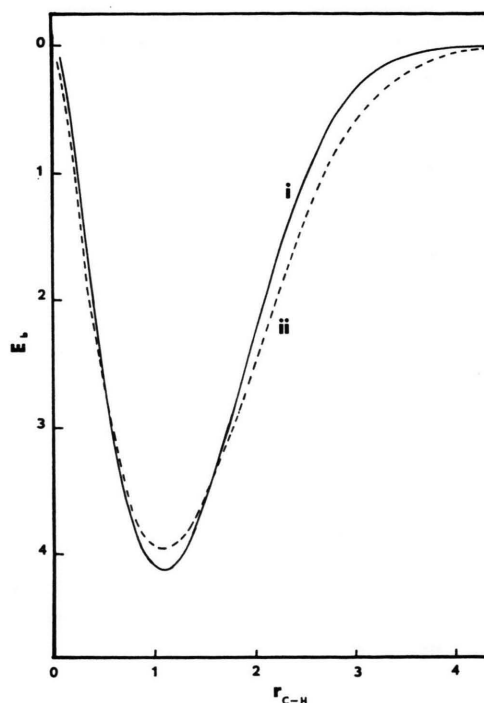
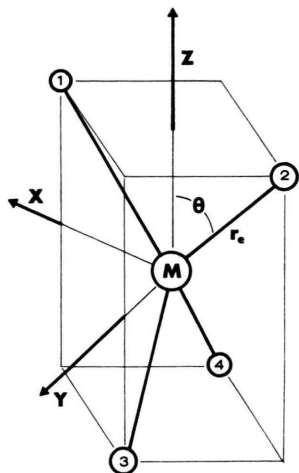
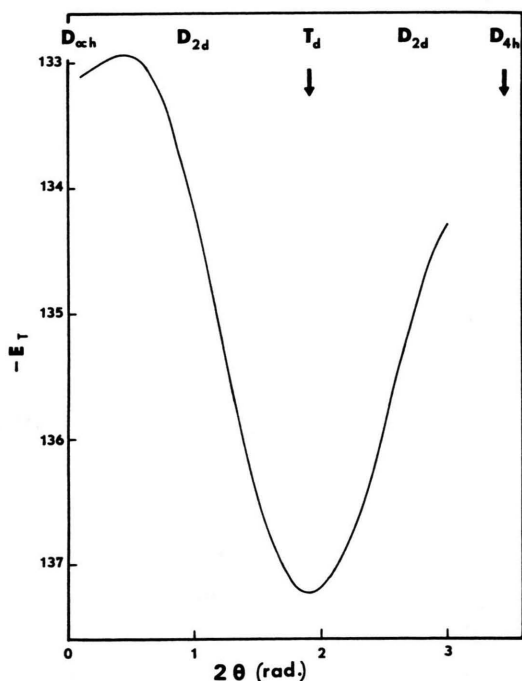


Fig. 3. The CH "Bond" Potential Energies (in eV).

### Angular Dependence of the Potential Energy

The encouraging results of the preceding sections, moreover, prompted us to examine the angular dependence of the total potential energy of the previously studied molecules. Fig. 4 gives the geometric set-up of the atoms involved, while Table V and VI give respectively the symmetry orbitals used in the  $D_{2d}$  limit and their corresponding group overlaps. As can be seen from Fig. 4 *all* the  $F_\sigma$ 's needed in this section were indeed transferable from our previous studies.

Fig. 4. Geometric Configuration of  $MH_4$  in the  $D_{2d}$  Model.Fig. 5. Angular Dependence of the Potential Energy of  $CH_4$ . The energy is in eV.

The results of our calculations for the methane molecule are displayed in Fig. 5 where the minimum of the potential is obtained at  $\theta = 54.75^\circ$ . It should be noted that similar curves were obtained for all the molecules studied. Unfortunately, however, these potential curves which did indeed give the correct geometry, were unable to reproduce the experimentally obtained angle bending force constants<sup>17</sup>.

### Determination of Potential Barriers

An interesting outcome of the previous section was the fact that the proportionality constants obtained by our recipe seemed to be atom-atom parameters, transferable from molecule to molecule. In the present section we extend our previous studies by using the latter concept in the semi-empirical determination of the geometries, as well as the inversion potential barriers, if any, of  $CH_3$ ,  $SiH_3$ ,  $NH_3$  and  $PH_3$ .

Using the group overlaps of Table III as well as the experimental internuclear distances given in Table VII, the total orbital energies of the molecules under consideration were determined as a

$$\begin{aligned}\langle ns | \Sigma(a_1) \rangle &= \sqrt{3} \langle ns | \sigma \rangle / [1 + X(a_1)]^{1/2} \\ \langle np_z | \Sigma(a_1) \rangle &= \sqrt{3} \cos \theta \langle np_\sigma | \sigma \rangle / [1 + X(a_1)]^{1/2} \\ \langle ns | \sigma_4 \rangle &= \langle ns | \sigma \rangle \\ \langle np_z | \sigma_4 \rangle &= \langle np_\sigma | \sigma \rangle \\ \langle np_x | \Sigma^a(e) \rangle &= \sqrt{6} \sin \theta \langle np_\sigma | \sigma \rangle / 2 [1 - X(e)]^{1/2} \\ \langle np_y | \Sigma^b(e) \rangle &= \sqrt{6} \sin \theta \langle np_\sigma | \sigma \rangle / 2 [1 - X(e)]^{1/2}\end{aligned}$$

$$\begin{aligned}\text{where } \sigma &\equiv 1 s_H \\ X(a_1) &\equiv 2 \langle \sigma_1 | \sigma_2 \rangle \\ X(e) &\equiv \langle \sigma_1 | \sigma_2 \rangle\end{aligned}$$

Table III. Group Overlap in  $C_{3v}$  Symmetry.

|          | Exp | Calc. I <sup>a</sup> | Calc. II <sup>b</sup> |
|----------|-----|----------------------|-----------------------|
| $CH_4$   | 4.3 | 4.2                  | 3.9                   |
| $SiH_4$  | 3.3 | 3.6                  | 1.9                   |
| $NH_4^+$ | —   | 2.6                  | 2.5                   |
| $PH_4^+$ | —   | 2.0                  | 1.8                   |

Table IV. Calculated and Observed Bond Energy Terms in eV. <sup>a</sup> From our previous note (Ref. 3); <sup>b</sup> Within the "diatomic" approximation.

function of the angle  $\Phi (\equiv \pi - \theta)$ . As can be seen from Fig. 6 and 7, the calculated minima for both the  $CH_3$  and  $SiH_3$  radicals occur at the  $D_{3h}$  symmetry (planar), while the  $NH_3$  and  $PH_3$  molecules are calculated to have an equilibrium  $C_{3v}$  symmetry. It is interesting to note that a recent calculation using Roothaan's SCF technique<sup>20</sup> and Gaussian-

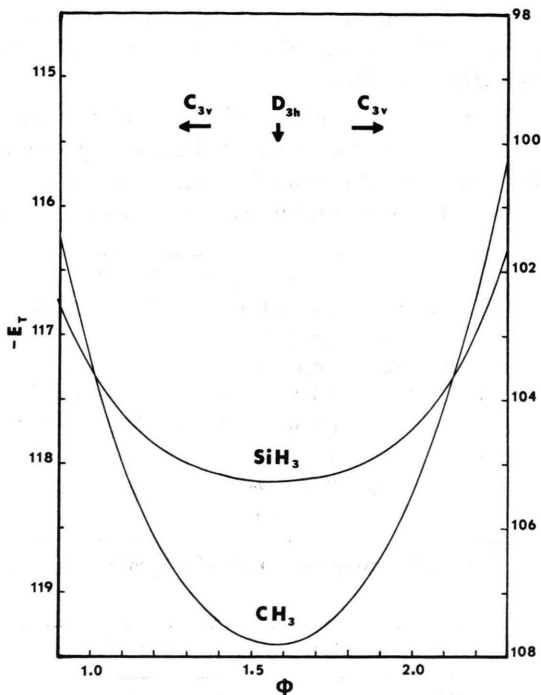
<sup>17</sup> The force constants  $f_\phi$  were found to be 1.3, 0.7, 0.7 and 0.2 md/A for  $CH_4$ ,  $SiH_4$ ,  $PH_4^+$  and  $NH_4^+$ , respectively.

<sup>18</sup> G. HERZBERG, Molecular Spectra and Molecular Structure, Vol. II, D. Van Nostrand Co., Inc., New York 1966.

<sup>19</sup> W. S. BODY and E. K. PLYLER, Can. J. Phys. **35**, 1235 (1957).

<sup>20</sup> R. G. BODY, D. S. MCCLURE, and E. CLEMENTI, J. Chem. Phys. **49**, 4916 [1968].

| Reps  | Orbitals on M | Hydrogen Symmetry Orbitals  |
|-------|---------------|---|
| $a_1$ | $ns$          | $\Sigma(a_1) = 2^{-1}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)/[1 + \langle \sigma_1   \sigma_2 \rangle + 2 \langle \sigma_1   \sigma_3 \rangle]^{1/2}$ |
| $b_2$ | $np_z$        | $\Sigma(b_2) = 2^{-1}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)/[1 + \langle \sigma_1   \sigma_2 \rangle - 2 \langle \sigma_1   \sigma_3 \rangle]^{1/2}$ |
| $e$   | $np_x$        | $\Sigma^a(e) = 2^{-1/2}(\sigma_1 - \sigma_2)/[1 - \langle \sigma_1   \sigma_2 \rangle]^{1/2}$   |
|       | $np_y$        | $\Sigma^b(e) = 2^{-1/2}(\sigma_3 - \sigma_4)/[1 - \langle \sigma_3   \sigma_4 \rangle]^{1/2}$   |

Table V. Symmetry orbitals in the  $D_{2d}$  Model.Fig. 6. "Total energies" of  $\text{CH}_3$  and  $\text{SiH}_3$  versus  $\phi$  ( $\equiv \pi - \theta$ ). The scale on the left is for  $\text{SiH}_3$ .

$$\begin{aligned} \langle ns | \Sigma(a_1) \rangle &= 2 \langle ns | \sigma \rangle / [1 + X(a_1)]^{1/2} \\ \langle np_z | \Sigma(b_2) \rangle &= 2 \cos \theta \langle np_z | \sigma \rangle / [1 + X(b_2)]^{1/2} \\ \langle np_x | \Sigma^a(e) \rangle &= 2^{1/2} \sin \theta \langle np_x | \sigma \rangle / [1 - X(e)]^{1/2} \\ \langle np_y | \Sigma^b(e) \rangle &= 2^{1/2} \sin \theta \langle np_y | \sigma \rangle / [1 - X(e)]^{1/2} \end{aligned}$$

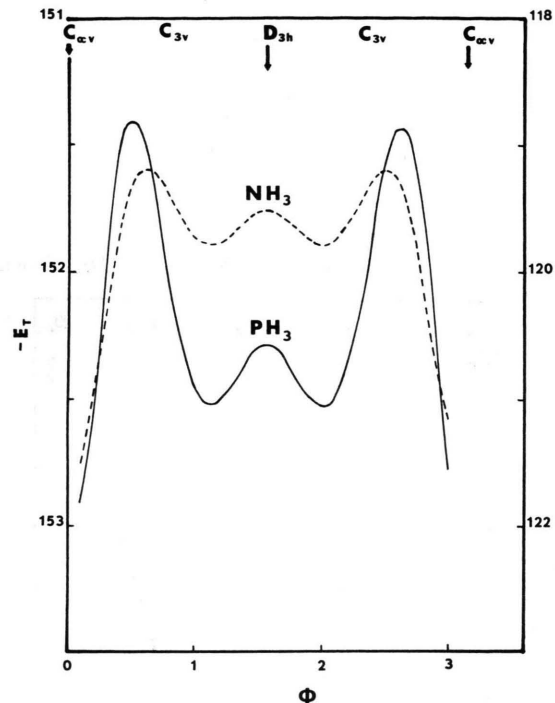
where

$$\begin{aligned} \sigma &= 1 s_H \\ X(a_1) &\equiv \langle \sigma_1 | \sigma_2 \rangle + 2 \langle \sigma_1 | \sigma_3 \rangle \\ X(b_2) &\equiv \langle \sigma_1 | \sigma_2 \rangle - 2 \langle \sigma_1 | \sigma_3 \rangle \\ X(e) &\equiv \langle \sigma_1 | \sigma_2 \rangle = \langle \sigma_3 | \sigma_4 \rangle \end{aligned}$$

Table VI. Group Overlaps in  $D_{2d}$  Symmetrie.

type s and p orbitals on nitrogen<sup>21</sup> gave an equilibrium geometry of  $r_{\text{NH}}^\circ = 0.996 \text{ \AA}$  and  $\alpha_{\text{HNN}}^\circ = 114.6^\circ$  with a potential barrier of approximately

<sup>21</sup> The addition of d-type functions to the basis set gives much better results for the equilibrium geometry and inversion barrier. Similar results may be expected in our calculations and in a future study we plan to investigate this point.

Fig. 7. "Total energies" of  $\text{NH}_3$  and  $\text{PH}_3$  versus  $\phi$ . The scale on the left is for  $\text{PH}_3$ .

0.03 eV. The results obtained by our simple-minded calculations, on the other hand, were  $1.04 \text{ \AA}$ ,  $104.5^\circ$ , and  $\sim 0.15 \text{ eV}$  respectively which compare favorably with the experimental values of  $1.01 \text{ \AA}$ ,  $106.7^\circ$  and  $\sim 0.25 \text{ eV}$ .

The present study suggests, moreover, that  $\text{NH}_3^+$  and  $\text{PH}_3^+$  should be planar (Fig. 8). It also suggests that  $\text{CH}_3^-$  will be planar and  $\text{SiH}_3^-$  will have an equilibrium  $C_{3v}$  symmetry with a very low ( $\cong 0.07 \text{ eV}$ ) potential barrier (Fig. 9). It is indeed interesting to note that although the geometry and potential barrier of  $\text{CH}_3^-$  has been the subject of several sophisticated investigations<sup>12,13</sup>, the problem seems as yet to be unresolved. In one of the last of these studies, for instance, Kari and Csizmadia report calculating a potential barrier of  $0.048 \text{ eV}$ , a value which seems to us to be highly questionable.

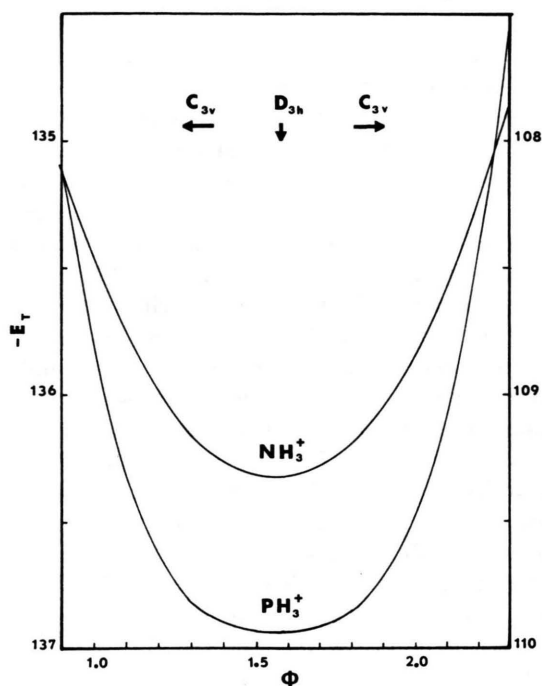


Fig. 8. "Total energies" of  $\text{NH}_3^+$  and  $\text{PH}_3^+$  versus  $\phi$ . The scale on the left is for  $\text{PH}_3^+$ .

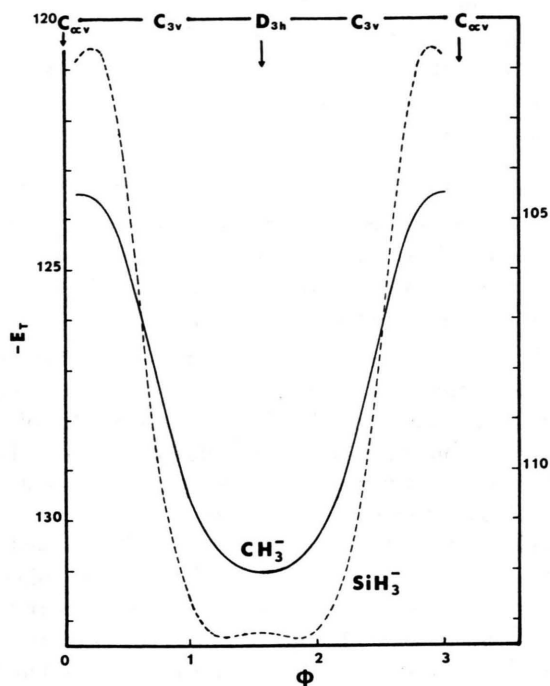


Fig. 9. "Total energies" of  $\text{CH}_3^-$  and  $\text{SiH}_3^-$  versus  $\phi$ . The scale on the left is for  $\text{CH}_3^-$ .

|                                  |     | $\text{CH}_3$ | $\text{SiH}_3$ | $\text{NH}_3$ | $\text{PH}_3$ |
|----------------------------------|-----|---------------|----------------|---------------|---------------|
| $r_0$                            | $E$ | 1.08 Å        | ?              | 1.01          | 1.42          |
|                                  | Y*  | 1.04          | 1.40           | 1.04          | 1.60          |
| $\angle \text{HMH}$              | $E$ | 120°          | 120            | 106.7         | 93.3          |
|                                  | Y   | 120           | 120            | 104.5         | 101.0         |
| Pot.                             | $E$ | 0 eV          | 0              | 0.25          | ~0.50         |
| Barr.                            | Y   | 0             | 0              | ~0.15         | ~0.50         |
| $\text{D}(\text{H}_2\text{M-H})$ | $E$ | ≤4.9 eV       | ?              | 4.4           | ?             |
|                                  | Y   | 4.7           | 4.5            | —             | —             |

Table VII. Calculated and Experimental\*\* Molecular Parameters of the Studied Molecules.

\* Determined from our calculated geometries.

\*\* All experimental values  $E$  were obtained from Ref.<sup>18</sup> except those of  $\text{NH}_3$  which were obtained from Ref.<sup>19</sup> Y stands for the calculated values.

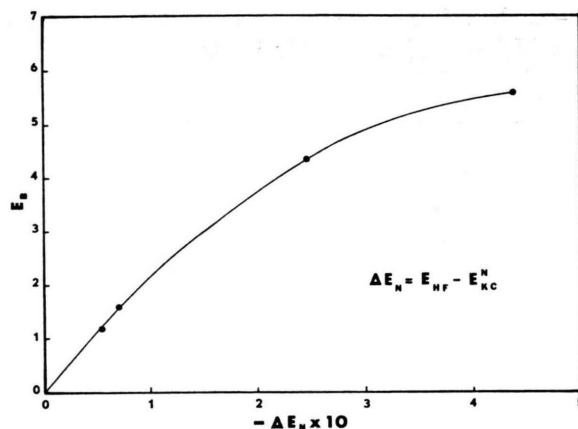


Fig. 10. Calculated Potential Barrier  $E_B$  (kcal/mole) versus  $\Delta E_N$  (Hartrees).  $\Delta E_N = E_{\text{HF}} - E_N$  (calculated by Kari & Csizmadia). The latter is a function of the number  $N$  of orbitals used in the basis set.

For, if one agrees with KARI and CSIZMADIA<sup>13</sup> that "one of the more significant observations from these calculations was that the barrier height of  $\text{CH}_3^-$  gradually decreased as the wave functions approached the Hartree-Fock limit", then, we suspect, as is seen in Fig. 10, that at the limit itself the potential barrier will be very nearly zero<sup>22</sup>; a prediction which agrees well with our simple-minded calculations.

<sup>22</sup> Another serious objection raised about Kari and Csizmadia's results is that their calculated simple valence field stretching force constants of both  $\text{CH}_3^+$  and  $\text{CH}_3^-$  seem to be quite high. The CH stretching force constant in the planar  $\text{CH}_3^+$ , for instance, is calculated to be twice the value of the one found in similarly "hybridized" ethylene molecule! We believe that not only is such an increase improbable but that, in principle, the simple valence force constants in both molecules should be close.

The computation of the bond dissociation energies of the above mentioned radicals and molecules deserves some comment. First, we would like to bring to the reader's attention that implicit in our original proposal was the fact that the electrons whose energy sum was believed to be simulating the behavior of the true internuclear potential function of a molecule were actually *participants* in bond formation<sup>23</sup>, and second, since the technique did not consider systems with non-binding orbitals, an extension was obviously in order.

It is, indeed, not very difficult to see that all bonding and non-bonding electrons must be considered in the determination of the *geometry* of a molecule, but what is not, as yet, clear to us is the effect on non-bonding electrons on the above-mentioned simulation. Fortunately, however, in the specific case of the planar  $\text{SiH}_3$  and  $\text{CH}_3$  radicals, the extension seemed rather straightforward. Since the  $p_z$  orbitals in the latter were perpendicular to the planes in which the dissociations were occurring the electrons in them were simply not considered in the energy sum. This was our way of saying that *the occupancy of the  $p_z$  orbital should have very little effect on the M-H dissociation energy*. In fact, the C—C dissociation energies<sup>24</sup> in both  $\text{H}_2\text{C}=\text{CH}_2$  and  $\text{H}_2\text{C}=\text{CH}_2^+$  differ only by 0.06%.

## Discussion

In the preceding pages we endeavored to show that, in general, the extended Hückel method, as modified by us, simulated reasonably well the behavior of the actual molecular energy throughout the *entire* range of internuclear distances. So much so that we proposed that the dissociation energy of a molecule be determined by taking the difference of the electronic energy sums at the equilibrium and infinite distances both calculated within our semi-empirical formalism. Furthermore, we showed and will show in the next paper in this series, that unlike Hoffmann's approach, our scheme gives reasonable values of potential barriers. In fact, all things considered we feel gratified by our results. This is naturally not to say that there is no room for improvement or that all the assumptions in the proposed modification seem justifiable or have been tested. If there is one thing that this study brought forth clearly, it is that the proportionality constants  $F_\sigma(\text{CH})$  need not be the same as  $F_\sigma(\text{CC})$ , or for that matter the latter need not be the same as  $F_\pi(\text{CC})$ . In the next paper of this series, we shall discuss this subject in detail.

<sup>23</sup> Whose energies were, obviously, considered in the calculation of dissociation energies.

<sup>24</sup> S. W. BENSON, J. Chem. Ed., **42**, No. 9 (1965).