[December, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (12), 3477—3479 (1979) 3477

Calculation of the H_4 Potental Energy Surface by a Semi-empirical Method

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(Received December 27, 1978)

A semi-empirical method recently proposed for the calculation of the potential energy surface of the H_3 system is extended to a larger polyatomic H_4 system. The energy formula is based on the valence-bond formulation and is expressed as functions of many multiple exchange integrals. These integrals can be decomposed into "diatomic" contributions by using the Mulliken approximation. The diatomic contributions are estimated from accurate values of the H_2 molecule. Calculations of the H_4 potential energy for the symmetric linear, linear equidistant, and square planar configurations are presented. The present method is of use for dynamical studies of the H_2+D_2 exchange reaction.

In a previous paper, the author has proposed a new semi-empirical method for the calculation of the H_3 potential surface,[1] and has shown that this simple method yields a satisfactory and useful surface when compared with Liu's detailed *ab initio* calculation of the H_3 system.[2] It is interesting to extend the method to the case of larger polyatomic systems. In the present note the application to the H_4 potential surface calculation is presented.

There have been many *ab initio* calculations of the H_4 system at its special configurations, and the results have been discussed in connection with the mechanism of the $H_2+D_2 \rightarrow 2HD$ exchange reaction. Experimental results for this reaction have often been interpreted in terms of a vibrational excitation mechanism,[3] which assumes a four-center H_4 transition state. The recent extensive *ab initio* calculation of Silver and Stevens (SS)[4] yielded potential barriers for the four-center transition state larger than the H_2 dissociation energy, which is in disagreement with the experimental activation energy, 42 kcal/mol.[3] Thus we are very much interested in the reaction dynamics study of the H_2+D_2 reaction, in order to examine the effect of vibrational activation on the reaction cross section. For such a study, we must have a complete reliable potential surface of the H_4 system. The author believes that the present note provides a practically useful method of calculating the surface, since it requires less computer time than *ab initio* calculations.

In the following section, we proceed in much the same way as the case of H_3.[1] By making use of the Mulliken approximation,[5] Slater's energy formula[6] is shown to be expressed in terms of "diatomic" contributions, *i.e.*, diatomic Coulomb (Q_i), exchange (α_i), and overlap (S_i) integrals. Hence we obtain the energy formula involving several empirical parameters. The surface thus calculated is compared with the results of the *ab initio* calculations of the H_4 surface,[4,7] in the last section.

Theoretical

Slater's energy formula[6] for the four-orbital four-electron system corresponding to H_4 is

$$E_{\pm} = (1/C_1)[-C_2 \pm (C_2^2 - C_1C_3)^{1/2}]. \qquad (1)$$

The quantities C_1, C_2, C_3 are expressed in terms of the matrix elements:

$$\begin{aligned} C_1 &= (\mathrm{I}|\mathrm{I})(\mathrm{II}|\mathrm{II}) - (\mathrm{I}|\mathrm{II})^2, \\ C_2 &= (\mathrm{I}|H|\mathrm{II})(\mathrm{I}|\mathrm{II}) - \frac{1}{2}\{(\mathrm{I}|H|\mathrm{I})(\mathrm{II}|\mathrm{II}) \\ &\quad - (\mathrm{II}|H|\mathrm{II})(\mathrm{I}|\mathrm{I})\}, \\ C_3 &= (\mathrm{I}|H|\mathrm{I})(\mathrm{II}|H|\mathrm{II}) - (\mathrm{I}|H|\mathrm{II}), \end{aligned} \qquad (2)$$

where the bond functions Ψ_{I} and Ψ_{II} correspond to the bonding schemes (a—b, c—d) and (a—d, b—c) respectively, and H is the Hamiltonian of the system,

$$H = \sum_{i=1}^{4}\left(-\frac{1}{2}\nabla_i^2 - \sum_{\nu=1}^{4}\frac{1}{r_{i\nu}} + \sum_{j>i}\frac{1}{r_{ij}}\right) + \sum_{\kappa=1}^{6}\frac{1}{R_\kappa}. \qquad (3)$$

The subscripts i, j refer to the electrons, ν=a, b, c, d represent the four hydrogen nuclei, and R_1, R_2, R_3, R_4, R_5, and R_6 are the a—b, a—c, a—d, b—c, b—d, and c—d internuclear distances respectively. In terms of the functions Ψ_{I} and Ψ_{II}, the matrix elements can be written as

$$\begin{aligned} (\mathrm{I}|H|\mathrm{I}) &= 4Q + 2(2\alpha_1' - \alpha_2' - \alpha_3' - \alpha_4' - \alpha_5' + 2\alpha_6') \\ &\quad + 4(\beta_{25} + \beta_{34} + \beta_{16}) - 4(\gamma_{214} + \gamma_{153} + \gamma_{326} + \gamma_{465}) \\ &\quad + 4(\delta_{2543} + \delta_{3425}) - 2(\delta_{1526} + \delta_{2165} + \delta_{3146} - \delta_{1463}), \\ (\mathrm{II}|H|\mathrm{II}) &= 4Q - 2(\alpha_1' + \alpha_2' - 2\alpha_3' - 2\alpha_4' + \alpha_5' + \alpha_6') \\ &\quad + 4(\beta_{16} + \beta_{25} + \beta_{34}) - 4(\gamma_{214} + \gamma_{465} + \gamma_{153} + \gamma_{326}) \\ &\quad + 4(\delta_{2165} + \delta_{1526}) - 2(\delta_{2543} + \delta_{3425} + \delta_{3146} + \delta_{1463}), \\ (\mathrm{II}|H|\mathrm{I}) &= -2Q - 2(\alpha_1' - 2\alpha_2' + \alpha_3' + \alpha_4' - 2\alpha_5' + \alpha_6') \\ &\quad - 2(\beta_{16} + \beta_{34} + \beta_{25}) + 2(\gamma_{465} + 2\gamma_{153} + \gamma_{326} + \gamma_{214} \\ &\quad - \gamma_{315} - \gamma_{546}) + 2(2\delta_{3146} + \delta_{1463} - \delta_{2165} - \delta_{1526} \\ &\quad - \delta_{2543} - \delta_{3425}), \\ (\mathrm{I}|\mathrm{I}) &= 2\{(1-S_2^2)(1-S_5^2) + (1-S_3^2)(1-S_4^2) \\ &\quad + (S_1S_6 - S_3S_4)^2 - 2(S_1 - S_3S_5)(S_2S_4 - S_1) \\ &\quad + (S_1S_6 - S_2S_5)^2 - 2(S_6 - S_2S_3)(S_4S_5 - S_6)\}, \\ (\mathrm{II}|\mathrm{II}) &= 2\{(1-S_1^2)(1-S_6^2) + (1-S_2^2)(1-S_5^2) \\ &\quad + (S_3S_4 - S_2S_5)^2 - 2(S_4 - S_1S_2)(S_5S_6 - S_4) \\ &\quad + (S_1S_6 - S_3S_4)^2 - 2(S_3 - S_2S_6)(S_1S_5 - S_3)\}, \\ (\mathrm{I}|\mathrm{II}) &= 2\{(S_4 - S_1S_2)(S_5S_6 - S_4) + (S_3 - S_1S_5)(S_2S_6 - S_3) \\ &\quad + (S_1 - S_3S_5)(S_2S_4 - S_1) + (S_6 - S_2S_3)(S_4S_5 - S_6) \\ &\quad - (S_2 - S_1S_4)(S_3S_6 - S_2) - (S_5 - S_4S_6)(S_1S_3 - S_5) \\ &\quad - (S_1S_6 - S_3S_4)^2 - (1-S_2^2)(1-S_5^2)\}, \end{aligned} \qquad (4)$$

where Q is the Coulomb integral, α_i' are single-exchange integrals, β_{ij} are double-exchange integrals, γ_{ijk} are triple-exchange integrals, δ_{ijkm} are quadruple-exchange integrals, and S_i are overlap integrals. These are defined by the relations,

$$\begin{aligned}
Q &= (\mathrm{abcd}|H|\mathrm{abcd}), \\
\alpha_1' &= (\mathrm{abcd}|H|\mathrm{bacd}), \quad S_1 = (\mathrm{a}|\mathrm{b}), \\
\alpha_2' &= (\mathrm{abcd}|H|\mathrm{cbad}), \quad S_2 = (\mathrm{a}|\mathrm{c}), \\
\alpha_3' &= (\mathrm{abcd}|H|\mathrm{dbca}), \quad S_3 = (\mathrm{a}|\mathrm{d}), \\
\alpha_4' &= (\mathrm{abcd}|H|\mathrm{acbd}), \quad S_4 = (\mathrm{b}|\mathrm{c}), \\
\alpha_5' &= (\mathrm{abcd}|H|\mathrm{adcb}), \quad S_5 = (\mathrm{b}|\mathrm{d}), \\
\alpha_6' &= (\mathrm{abcd}|H|\mathrm{abdc}), \quad S_6 = (\mathrm{c}|\mathrm{d}), \\
\beta_{16} &= (\mathrm{abcd}|H|\mathrm{badc}), \\
\beta_{25} &= (\mathrm{abcd}|H|\mathrm{cdab}), \\
\beta_{34} &= (\mathrm{abcd}|H|\mathrm{dcba}), \\
\gamma_{142} &= (\mathrm{abcd}|H|\mathrm{bcad}) = \gamma_{214}, \\
\gamma_{153} &= (\mathrm{abcd}|H|\mathrm{bdca}), \\
\gamma_{263} &= (\mathrm{abcd}|H|\mathrm{cbda}) = \gamma_{326}, \\
\gamma_{315} &= (\mathrm{abcd}|H|\mathrm{dacb}), \\
\gamma_{465} &= (\mathrm{abcd}|H|\mathrm{acdb}) = \gamma_{546}, \\
\delta_{2165} &= (\mathrm{abcd}|H|\mathrm{cadb}) = \delta_{1526}, \\
\delta_{1463} &= (\mathrm{abcd}|H|\mathrm{bcda}) = \delta_{3146}, \\
\delta_{2543} &= (\mathrm{abcd}|H|\mathrm{cdba}) = \delta_{3425}.
\end{aligned} \tag{6}$$

The Coulomb integral Q is written as a sum of the diatomic Coulombic contributions Q_i:

$$Q = 4E_{\mathrm{H}} + \sum_{i=1}^{6} Q_i, \tag{7}$$

where E_{H} represents the energy of a hydrogen atom.

The exchange integrals α_i', β_{ij}, γ_{ijk}, and δ_{ijkm} can also be decomposed into "diatomic" contributions Q_i, α_i, and S_i by using the Mulliken approximation:[5)]

$$\begin{aligned}
\alpha_i' &\simeq \alpha_i + S_i^2(Q - Q_i), \\
\beta_{ij} &\simeq S_i^2 S_j^2 \{\alpha_i/S_i^2 + \alpha_j/S_j^2 + (Q - Q_i - Q_j)\}, \\
\gamma_{ijk} &\simeq \frac{1}{2} S_i S_j S_k \{\alpha_i/S_i^2 + \alpha_j/S_j^2 + \alpha_k/S_k^2 + 2Q \\
&\quad - (Q_i + Q_j + Q_k)\}, \\
\delta_{ijkm} &\simeq \frac{1}{2} S_i S_j S_k S_m \{\alpha_i/S_i^2 + \alpha_j/S_j^2 + \alpha_k/S_k^2 + \alpha_m/S_m^2 \\
&\quad + 2Q - (Q_i + Q_j + Q_k + Q_m)\}.
\end{aligned} \tag{8}$$

Eventually, the energy, Eq. 1, is evaluated in terms of the diatomic integrals Q_i, α_i, and S_i. Following Porter and Karplus,[8)] we write the Q_i, α_i, and S_i as

$$\begin{aligned}
Q_i &= [(E^1 + E^3) + S_i^2(E^1 - E^3)]/2, \\
\alpha_i &= [(E^1 - E^3) + S_i^2(E^1 + E^3)]/2,
\end{aligned} \tag{9}$$

where

$$\begin{aligned}
E^1 &= D_1\{\exp[-2\alpha(R_i - R_e)] - 2\exp[-\alpha(R_i - R_e)]\}, \\
E^3 &= D_3\{\exp[-2\beta(R_i - R_e)] + \exp[-\beta(R_i - R_e)]\},
\end{aligned} \tag{10}$$

and

$$S_i = (1 + \zeta_i R_i + \zeta_i^2 R_i^2/3)\exp(-\zeta_i R_i), \tag{11a}$$

where

$$\zeta_i = 1.0 + \kappa \exp(-\lambda R_i). \tag{11b}$$

Results and Discussion

Table 1. The parameters used to calculate the H_4 potential energy[a)]

$D_1 = 0.174475$ a.u.	$\kappa = 1.00$
$D_3 = 0.072900$ a.u.	$\lambda = 0.40$
$\alpha = 1.050000$ a.u.$^{-1}$	
$\beta = 1.036000$ a.u.$^{-1}$	
$R_e = 1.401000$ a.u.	

a) For definitions see the text.

Table 2. Comparison of the values of the screening parameter ζ_i

R_i	ζ_i (present paper)	ζ_i (Porter and Karplus)
1.5	1.549	1.226
2.0	1.449	1.164
2.5	1.368	1.118
3.0	1.301	1.085
4.0	1.202	1.045
5.0	1.135	1.023
6.0	1.091	1.012

The parameters D_1, D_3, α, β, and R_e in Eqs. 10 have been determined from the results of the accurate *ab initio* calculation on H_2 by Kołos and Wolniewicz[9)] (see Ref. 1 for details). The screening parameter ζ_i appearing in Eq. 11a for the overlap integral S_i is given as a function of the internuclear distance R_i by Eq. 11b, which involves two parameters κ and λ. In their calculation of the H_3 system, Porter and Karplus[8)] determined the values of κ and λ from early calculations of the H_2 molecule by Wang and Rosen.[10)] In the present paper, however, κ and λ have been determined by fitting Eq. 1 to the *ab initio* calculations on the linear symmetric H_4 by Bender and Schaefer III (BS).[7)] The values of the parameters thus determined are shown in Table 1. The values of the screening parameter ζ_i determined by Eq. 11b with the values of κ and λ in Table 1 are slightly higher than the values of ζ_i by Porter and Karplus (Table 2). This difference of the two sets of ζ_i values seems to be due to the difference

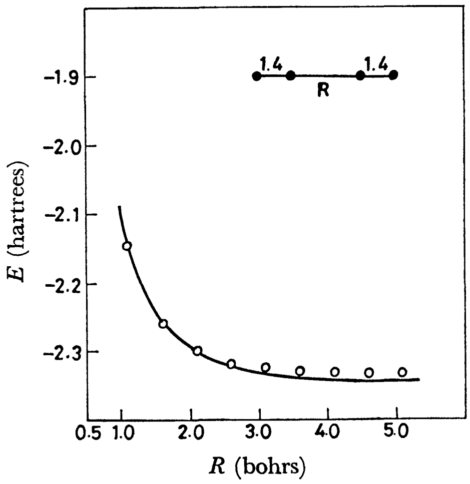

Fig. 1. Potential energies of symmetric linear H_4 as a function of distance of approach R with two H_2 molecule at equilibrium.
BS oooo;[7)] ——, the present work.

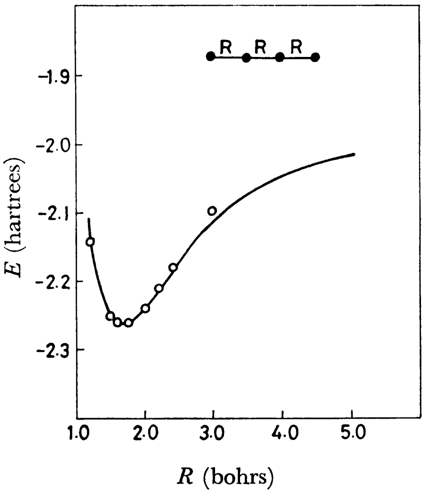

Fig. 2. Potential energies of linear equidistant H_4 as a function of *R*. *R* is the distance between H atoms. BS oooo;[7] ——, the present work.

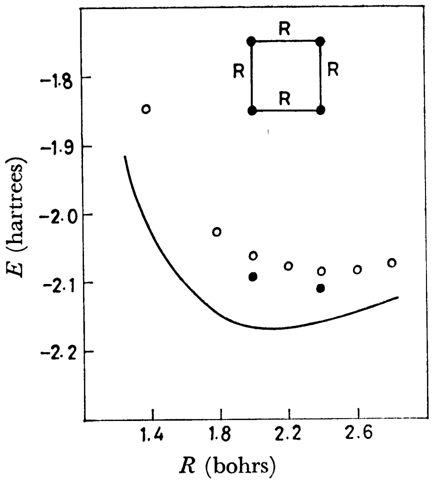

Fig. 3. Potential energies for square planar H_4. *R* measures the side of the square.
SS oooo, used orbital basis s,s′; SS ••••, used orbital basis s,s′, p;[4)— , the present work.

in the methods by which the values of κ and λ have been determined (see above).

In the case of linear symmetric and linear equidistant configurations, the results obtained here are compared with those of BS[7] in Figs. 1 and 2: The agreement is satisfactory. A similar calculation for square planar configuration is shown in Fig. 3, where we compare the results with those of SS.[4] The agreement is not so good as in the case of Figs. 1 and 2. It should be remembered that the values of κ and λ have been adjusted for the linear symmetric H_4. However it does not seem worthwhile to try to improve the above disagreement by readjusting the values of κ and λ for the square H_4, because the precision of the SS calculation is not as high as that of the BS calculation. In fact, it has been pointed out that the SS energies can be lowered by more than 0.025 hartrees by extending the orbital basis and by optimizing the orbital exponents.[4]

The author wishes to thank Professor T. Nakamura of Hokkaido University for many helpful discussions and suggestions. The numerical calculations were performed on the FACOM 230-75 computer at the Hokkaido University Computing Center.

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