FSGO Open-shell Calculations on Linear Triatomic and Tetra-atomic Hydrogen Complexes

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Summary FSGO calculations on linear arrangements of hydrogen atoms are reported; the hydrogen atom, but not the hydrogen molecule, could stabilize the H_3 transition state in the $H + H_2 \rightarrow H_2 + H$ exchange reaction.

THE Floating Spherical Gaussian Orbital (FSGO) model has been adapted for open-shell calculations and used with success on one-, two-, and three-electron systems.[1,2] Of particular interest is the $H + H_2 \rightarrow H_2 + H$ exchange

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reaction, one of the simplest chemical processes, for which the transition state (H_3) is predicted to be linear and symmetric, in agreement with other *ab initio* calculations.[3,4] For H_3 treated as a three-electron system occupying open-shell orbitals a, b, and c, with the orbitals fixed to the nuclei, the optimised energy[2] calculated from the three-determinant wavefunction (1) of the linear symmetric H_3 in its doublet state is $-1{\cdot}3890$ a.u.‡ with an r (H–H)

$$\psi = C_1|\bar{\phi}_a\phi_b\phi_c| + C_2|\phi_a\bar{\phi}_b\phi_c| + C_3|\phi_a\phi_b\bar{\phi}_c| \tag{1}$$

internuclear distance of 1·9080 a.u.‡ (see Table).

We have now carried out an analogous calculation for linear H_4 in its singlet state, based on the open-shell FSGO six-determinant wavefunction (2), with the four electrons

$$\begin{aligned}\psi = {} & C_1|\phi_a\bar{\phi}_b\phi_c\bar{\phi}_d| + C_2|\bar{\phi}_a\phi_b\bar{\phi}_c\phi_d| + C_3|\bar{\phi}_a\phi_b\phi_c\bar{\phi}_d| \\ & + C_4|\phi_a\bar{\phi}_b\bar{\phi}_c\phi_d| + C_5|\phi_a\phi_b\bar{\phi}_c\bar{\phi}_d| + C_6|\bar{\phi}_a\bar{\phi}_b\phi_c\phi_d|\end{aligned} \tag{2}$$

singly occupying the four orbitals a, b, c, and d which are fixed to the nuclei. The optimised energies for various linear configurations of H_4 (H–H–H · · · · H) were calculated as a function of the $H_3 \cdots\cdots H$ distance, with the symmetric linear H_3 (H–H–H) unit fixed at the internuclear distance r (H–H) of 1·9080 a.u. The resultant energy curve showed a pronounced minimum ($-1{\cdot}9176$ a.u.) at an r ($H_3 \cdots\cdots H$) distance of 1·5846 a.u. This result suggests that hydrogen atoms could act as catalysts of the exchange reaction $H + H_2 = H_2 + H$ by lowering the energy of the H_3 transition state. It would not be necessary for the hydrogen atom to be very close to the H_3 complex to exert some stabilising effect. The calculated binding energy of H_3 and H is 0·1042 a.u. (273·6 kJ mol^{-1}). The above hydrogen exchange reaction is followed by isotopic exchange or by *ortho–para* conversion. The rate of the above exchange reaction is proportional to $[H][H_2]$. If there were a catalytic effect, there would be added to this a term proportional to $[H]^2[H_2]$; this would be associated with a lower activation energy than the uncatalysed process, and this activation energy could be zero. However, it could only compete with the uncatalysed process at high concentrations of hydrogen atoms. Even at 1400 K, it has been estimated[5] that the maximum concentration of hydrogen atoms generated under typical shock tube conditions is extremely small, being only *ca.* 10^{-15} mol cm^{-3}. However, it is possible that the catalysed reaction might have some importance under plasma conditions or in hydrogen–oxygen flames where much higher temperatures occur and the hydrogen atom concentration is consequently higher.

TABLE

FSGO open-shell energies for the free hydrogen atom and linear di-, tri-, and tetra-atomic hydrogen molecules or complexes.[a]

System	Energy/a.u.	Internuclear distance/a.u.
H	$-0{\cdot}4244^{b}$	—
H_2	$-0{\cdot}9869^{c}$	1·5450
H_3 (symmetric) . .	$-1{\cdot}3890^{c}$	$1{\cdot}9080^{c}$
$H_3 + H$	$-1{\cdot}8134$	—
$H_3{\cdot}H$	$-1{\cdot}9176$	1·9080 for H · · H · · · H 1·5846 for H_3 · · · H

[a] All calculations were performed with the orbitals fixed to their respective nuclei. [b] A. H. Pakiari, Ph.D. Thesis, Cambridge, 1974. [c] L. P. Tan, Ph.D. Thesis, Cambridge, 1974.

The question then arises as to whether the hydrogen molecule could act as a catalyst for the exchange reaction. To investigate this, open-shell FSGO calculations of the optimised energies of the linear system of five hydrogen atoms were performed for different $H_3 \cdots\cdots H_2$ distances, using an appropriate ten-determinant wavefunction. The results of these calculations, in which the internuclear distances for H_3 and H_2 given in the Table were used, did not show any stabilisation of H_3 by H_2. This was also true of calculations for perpendicular or parallel modes of approach between H_3 and H_2.

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‡ 1 a.u. of energy ≡ $4{\cdot}3598 \times 10^{-18}$ J; 1 a.u. of distance ≡ $0{\cdot}5292 \times 10^{-10}$ m.

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