

Commentationes

Ab initio Calculation on the H₃ Activated Complex

A. RIERA and J. W. LINNETT

Department of Physical Chemistry, Cambridge

Received June 10, 1969

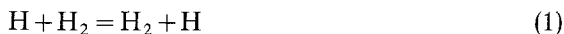
A full configuration interaction treatment has been carried out for linear, symmetrical H₃ activated complex, with a limited basis set of Slater orbitals. A similar calculation is performed on H₂ in order to obtain an estimate of the activation energy of the reaction $H + H_2 = H_2 + H$. The variation of non-linear parameters in the basis set is studied and the different behaviour of the H₃ and H₂ resulting wave functions examined. — A larger basis set is needed.

Eine vollständige CI-Behandlung wurde für einen linearen, symmetrischen, aktivierten H₃-Komplex mit einem begrenzten Basissatz von Slaterorbitalen durchgeführt. Eine ähnliche Rechnung wird für H₂ ausgeführt, um eine Abschätzung der Aktivierungsenergie der Reaktion $H + H_2 = H_2 + H$ zu erhalten. Die Variation von nichtlinearen Parametern im Basissatz wird untersucht und das verschiedenartige Verhalten der resultierenden H₃ und H₂ Wellenfunktion überprüft. — Ein größerer Basissatz wird benötigt!

Interaction de configurations totale pour le complexe activé H₃ linéaire et symétrique, dans une base limitée d'orbitales de Slater. Un calcul analogue a été effectué sur H₂ afin d'évaluer l'énergie d'activation de la réaction $H + H_2 = H_2 + H$. La variation des paramètres non linéaires de la base est étudiée, et l'on examine le comportement différent des fonctions d'onde de H₃ et de H₂. Une base plus étendue serait nécessaire.

Introduction

In this work, an attempt was made to compute a reasonably good wave function for the system of three electrons moving in the presence of three fixed nuclei, in the Born-Oppenheimer approximation, corresponding to the activated complex of the reaction:



with the standard method of superposition of configurations. A study was made of the importance of the variation of non-linear parameters in the basis set. This system has been studied by several authors [1]; the resulting wave functions are being used as a starting point for further calculations. For comparison purposes, and in order to obtain an estimate of the activation energy of this reaction, a parallel treatment was carried out for the H₂ molecule.

In the Born-Oppenheimer approximation, solution of the corresponding "Schrödinger equation" for each nuclear configuration gives one value for the "energy" or potential for the nuclear motion. This gives a function E defined in the three-dimensional space of co-ordinates R_{12} , R_{23} , and R_{13} where these symbols stand for the internuclear distances (see Fig. 1). From published work [1] we know that the activated complex of the reaction (1) corresponds to a linear symmetrical configuration of the three nuclei; therefore only this case was studied here.

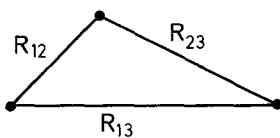
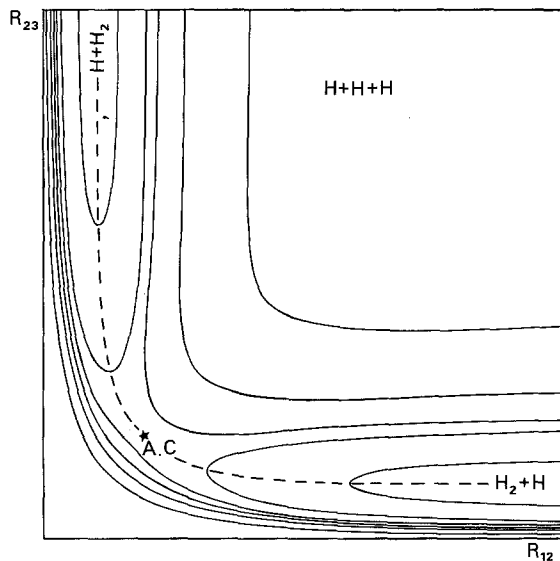


Fig. 1. Conventions for internuclear co-ordinates

Fig. 2. Energy contours for the surface $E(R_{12}, R_{23})$. $A.C.$ is the saddle point corresponding to the activated complex. The "reaction path" is indicated by a broken line

If we consider the linear system of three hydrogen atoms, i.e. if we impose the constraint $R_{13} = R_{12} + R_{23}$ we obtain a function E defined on the plane (R_{12}, R_{23}) . A qualitative picture of it is given in Fig. 2. The activated complex, which we shall call the H_3 system, corresponds to a saddle point on this surface $E(R_{12}, R_{23})$. Its energy is a minimum in the symmetrical normal co-ordinate studied here ($R = R_{12} = R_{23}$) as well as in the other normal co-ordinates, except the anti-symmetrical one, for which it is a maximum; its height relative to the horizontal plane corresponding to the energy of the reactants is the classical activation energy of the above reaction (i.e. not including zero-point vibrational corrections).

Calculation

We have studied the line on the energy surface $E(R_{12}, R_{23})$ corresponding to the further restriction $R_{12} = R_{23}$. Hence we were able to make use of the symmetry of the system to reduce considerably the number of different two-electron integrals (none of which was neglected or approximated). Linear symmetrical H_3 belongs to the point group $D_{\infty h}$ (for character table, see Ref. [2], page 388), and we need only consider all those terms in the expansion which transform like the irreducible representation Σ_u^+ . Most probably this corresponds to the (doublet) ground state of H_3 , hence reducing the size of the secular equation. The same group theoretical considerations apply to H_2 , whose ground state is a singlet of symmetry Σ_g^+ .

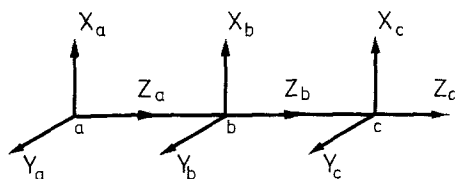
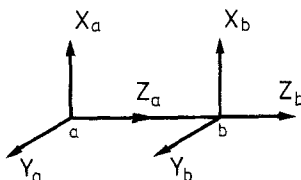
Fig. 3. Conventions for the system of axis for the linear symmetrical H₃ system

Fig. 4. Conventions for the system of axis for the hydrogen molecule

The one-electron orbital basis set for H₃ was taken to be one “1s” and three “2p” Slater orbitals centered on each nucleus:

$$\begin{aligned}
 1s_i &= \frac{\alpha^{3/2}}{\pi^{1/2}} \exp(-\alpha r_i), \\
 2p_{x_i} &= \frac{\alpha^{5/2}}{\pi^{1/2}} \beta^{5/2} \exp(-\alpha\beta r_i) r_i \sin\theta_i \cos\phi, \\
 2p_{y_i} &= \frac{\alpha^{5/2}}{\pi^{1/2}} \beta^{5/2} \exp(-\alpha\beta r_i) r_i \sin\theta_i \sin\phi, \\
 2p_{z_i} &= \frac{\alpha^{5/2}}{\pi^{1/2}} \beta^{5/2} \exp(-\alpha\beta r_i) r_i \cos\theta_i,
 \end{aligned} \tag{2}$$

where $i = a, b, c$, and the labelling of the nuclei and the conventions for the axis systems are as in Fig. 3.

For H₂ the basis set is also given by (2), where $i = a, b$, and the conventions are as in Fig. 4. The use of the product $\alpha\beta$ in the exponent of the p orbitals in (2) is due to reasons which will become clear when the variation of these non-linear parameters is described.

In both cases the simplest combinations transforming like the irreducible representations of $D_{\infty h}$ were chosen from these orbitals; these combinations are given in Table 1. These sets were orthonormalized by applying the transformation

Table 1. Combinations of the atomic basis set transforming like the irreducible representations of $D_{\infty h}$

a) H ₃ system			
$1s_a + 1s_c$	$2p_{x_a} + 2p_{x_c}$	$2p_{y_a} + 2p_{y_c}$	$2p_{z_a} + 2p_{z_c}$
$\left. \begin{array}{l} \sigma_y^+ \\ 1s_b \end{array} \right\}$	$\left. \begin{array}{l} \pi_u \\ 2p_{x_b} \end{array} \right\}$	$\left. \begin{array}{l} \pi_u \\ 2p_{y_b} \end{array} \right\}$	$\left. \begin{array}{l} \sigma_u^+ \\ 2p_{z_b} \end{array} \right\}$
$1s_a - 1s_c$	$2p_{x_a} - 2p_{x_c}$	$2p_{y_a} - 2p_{y_c}$	$2p_{z_a} - 2p_{z_c}$
$\left. \begin{array}{l} \sigma_u^+ \\ \end{array} \right\}$	$\left. \begin{array}{l} \pi_y \\ \end{array} \right\}$	$\left. \begin{array}{l} \pi_y \\ \end{array} \right\}$	$\left. \begin{array}{l} \sigma_y^+ \\ \end{array} \right\}$
b) H ₂ molecule			
$1s_a + 1s_b$	$2p_{x_a} + 2p_{x_b}$	$2p_{y_a} + 2p_{y_b}$	$2p_{z_a} + 2p_{z_b}$
$\left. \begin{array}{l} \sigma_u^+ \\ 1s_a - 1s_b \end{array} \right\}$	$\left. \begin{array}{l} \pi_u \\ 2p_{x_a} - 2p_{x_b} \end{array} \right\}$	$\left. \begin{array}{l} \pi_u \\ 2p_{y_a} - 2p_{y_b} \end{array} \right\}$	$\left. \begin{array}{l} \sigma_u^+ \\ 2p_{z_a} - 2p_{z_b} \end{array} \right\}$
$\left. \begin{array}{l} \sigma_u^+ \\ \end{array} \right\}$	$\left. \begin{array}{l} \pi_y \\ \end{array} \right\}$	$\left. \begin{array}{l} \pi_y \\ \end{array} \right\}$	$\left. \begin{array}{l} \sigma_y^+ \\ \end{array} \right\}$

Table 2a. Coefficients of the orthonormal one-electron basis set in terms of the atomic orbitals, for some values of (α, β, R) near the optimum one. The orthonormal set is numbered from 1 to 12 and these numbers correspond to those used in Table 3

	$1s_a$	$1s_b$	$1s_c$	$2p_{x_a}$	$2p_{x_b}$	$2p_{x_c}$	$2p_{y_a}$	$2p_{y_b}$	$2p_{y_c}$	$2p_{z_a}$	$2p_{z_b}$	$2p_{z_c}$
1	0.29571	0.22746	0.29571	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.32240	0.00000	-0.32240
2	-0.84728	2.23883	-0.84728	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.80241	0.00000	0.80241
3	0.37284	0.00000	-0.37284	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.29517	-0.28914	-0.29517
4	0.00000	0.00000	0.00000	0.45547	0.26271	0.45547	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
5	0.00000	0.00000	0.00000	-1.38929	2.40867	-1.38929	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6	0.00000	0.00000	0.00000	0.89314	0.00000	-0.89314	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
7	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.45547	0.26271	0.45547	0.00000	0.00000	0.00000
8	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-1.38929	2.40867	-1.38929	0.00000	0.00000	0.00000
9	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.89314	0.00000	-0.89314	0.00000	0.00000	0.00000
10	0.52832	0.00000	-0.52832	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.94742	-0.28593	0.94742
11	1.68759	0.00000	-1.68759	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.21736	2.39798	-0.21736
12	-0.57590	-0.02285	-0.57590	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.54435	0.00000	-0.54435
1) $\alpha = 1.18, \beta = 5/6, R = 1.771$ a.u.												
1	0.28730	0.22936	0.28730	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.33457	0.00000	-0.33457
2	-0.78306	2.12563	-0.78306	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.78478	0.00000	0.78478
3	0.39042	0.00000	-0.39042	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.28076	-0.29365	-0.28076
4	0.00000	0.00000	0.00000	0.46039	0.26680	0.46039	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
5	0.00000	0.00000	0.00000	-1.29593	2.23620	-1.29593	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6	0.00000	0.00000	0.00000	0.87089	0.00000	-0.87089	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
7	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.46039	0.26680	0.46039	0.00000	0.00000	0.00000
8	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-1.29593	2.23620	-1.29593	0.00000	0.00000	0.00000
9	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.87089	0.00000	-0.87089	0.00000	0.00000	0.00000
10	0.45759	0.00000	-0.45759	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.93669	-0.28721	0.93669
11	1.63225	0.00000	-1.63225	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.10207	2.26768	-0.10207
12	-0.58289	-0.02389	-0.58289	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.51692	0.00000	-0.51692
2) $\alpha = 1.18, \beta = 5/6, R = 1.864$ a.u.												

Table 2a (continued)

	1s _a	1s _b	1s _c	2p _{x_a}	2p _{y_a}	2p _{z_a}	2p _{x_b}	2p _{y_b}	2p _{z_b}	2p _{x_c}	2p _{y_c}	2p _{z_c}
3) $\alpha = 1.18, \beta = 1, R = 1.771$ a.u.												
1	0.28469	0.23144	0.28469	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.33294	0.00000	-0.33294
2	-0.95225	2.39699	-0.95225	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.85200	0.00000	0.85200
3	0.42465	0.00000	-0.42465	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.25771	-0.30609	-0.25771
4	0.00000	0.00000	0.00000	0.47485	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
5	0.00000	0.00000	0.00000	-1.09089	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6	0.00000	0.00000	0.00000	0.82236	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
7	0.00000	0.00000	0.00000	0.00000	0.47485	0.00000	0.27720	0.47485	0.00000	0.00000	0.00000	0.00000
8	0.00000	0.00000	0.00000	0.00000	0.00000	-1.09089	1.86872	0.00000	0.00000	0.00000	0.00000	0.00000
9	0.00000	0.00000	0.00000	0.00000	0.00000	0.82236	0.00000	-0.82236	0.00000	-0.82236	0.00000	0.00000
10	0.27137	0.00000	-0.27137	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.89738	-0.37907	0.89738
11	2.07251	0.00000	-2.07251	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.43362	2.51018	0.43362
12	-0.55391	-0.04146	-0.55391	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.50245	0.00000	-0.50245
4) $\alpha = 1.18, \beta = 1, R = 1.864$ a.u.												
1	0.27828	0.23487	0.27828	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.34417	0.00000	-0.34417
2	-0.87488	2.25059	-0.87488	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.82844	0.00000	0.82844
3	0.44227	0.00000	-0.44227	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	-0.23694	-0.31006	-0.23694
4	0.00000	0.00000	0.00000	0.48135	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
5	0.00000	0.00000	0.00000	-1.02174	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6	0.00000	0.00000	0.00000	0.80640	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
7	0.00000	0.00000	0.00000	0.00000	0.48135	0.00000	0.28106	0.48135	0.00000	0.00000	0.00000	0.00000
8	0.00000	0.00000	0.00000	0.00000	0.00000	-1.02174	1.74982	0.00000	0.00000	0.00000	0.00000	0.00000
9	0.00000	0.00000	0.00000	0.00000	0.00000	0.80640	0.00000	-0.80640	0.00000	-0.80640	0.00000	0.00000
10	0.21639	0.00000	-0.21639	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.87233	-0.35794	0.87233
11	1.95817	0.00000	-1.95817	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.50273	2.40896	0.50273
12	-0.56176	-0.04090	-0.56176	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.48214	0.00000	-0.48214

Table 2b. Coefficients of the orthonormal one-electron basis set of H in terms of the atomic orbitals. The orthonormal set is numbered from 1 to 8 and these numbers correspond to those used in Table 3 b

	$1s_a$	$1s_b$	$2p_{x_a}$	$2p_{x_b}$	$2p_{y_a}$	$2p_{y_b}$	$2p_{z_a}$	$2p_{z_b}$
1) $\alpha = 1.19, \beta = 1.5, R = 1.412$ a.u.								
1	0.44414	0.44414	0.00000	0.00000	0.00000	0.00000	0.24140	-0.24140
2	2.98528	-2.98528	0.00000	0.00000	0.00000	0.00000	1.62259	1.62259
3	0.00000	0.00000	0.56372	0.56372	0.00000	0.00000	0.00000	0.00000
4	0.00000	0.00000	1.08266	-1.08266	0.00000	0.00000	0.00000	0.00000
5	0.00000	0.00000	0.00000	0.00000	0.56372	0.56372	0.00000	0.00000
6	0.00000	0.00000	0.00000	0.00000	1.08266	-1.08266	0.00000	0.00000
7	-0.29855	0.29855	0.00000	0.00000	0.00000	0.00000	0.54928	0.54928
8	-0.39776	-0.39776	0.00000	0.00000	0.00000	0.00000	0.73181	-0.73181
2) $\alpha = 1.19, \beta = 1.5, R = 1.422$ a.u.								
1	0.44343	0.44343	0.00000	0.00000	0.00000	0.00000	0.24300	-0.24300
2	2.94222	-2.94222	0.00000	0.00000	0.00000	0.00000	1.61230	1.61230
3	0.00000	0.00000	0.56445	0.56445	0.00000	0.00000	0.00000	0.00000
4	0.00000	0.00000	1.07749	-1.07749	0.00000	0.00000	0.00000	0.00000
5	0.00000	0.00000	0.00000	0.00000	0.56445	0.56445	0.00000	0.00000
6	0.00000	0.00000	0.00000	0.00000	1.07749	-1.07749	0.00000	0.00000
7	-0.30098	0.30098	0.00000	0.00000	0.00000	0.00000	0.54925	0.54925
8	-0.39899	-0.39899	0.00000	0.00000	0.00000	0.00000	0.72810	-0.72810

obtained by diagonalizing the overlap matrix by the Jacobi process, and dividing by the square roots of the corresponding eigenvalues. The coefficients of the resultant 12 orbitals for the H_3 system and 8 orbitals for H_2 are given in Table 2 for some values of (α, β, R) . The choice of these values will be explained at the end of the description of the calculation.

The next stage in the calculation was the construction from these orbitals of all possible Slater determinants for which $S_z = 1/2$ for H_3 and $S_z = 0$ for H_2 , and from these to form all the orthonormal combinations which transform like the irreducible representation Σ_u^+ for H_3 and Σ_g^+ for H_2 , and for which $S = 1/2$ for H_3 and $S = 0$ for H_2 (readily obtained by means of Clebsch-Gordon coefficients). This set is given in Table 3a and b for H_3 and H_2 , respectively.

Finally, for several values of R and fixed values of α and β , the Hamiltonian matrix was set up in this representation, and diagonalized, obtaining an approximate ground state wave function with the lowest energy value possible using our atomic orbital basis set, for these values of α and β . Then, the importance of the variation of these non-linear parameters α and β was studied. For the variation with α use was made of the scaling technique, in order to avoid re-computing the matrix elements. Let γ be the scaling parameter, so that $\alpha' = \alpha\gamma$. Separate the Hamiltonian matrix corresponding to a distance R and a value of α into a "kinetic energy" part and a "potential energy" part:

$$H = T + V$$

where $T = -\frac{1}{2} \sum_{i=1}^3 \nabla_i^2$ and $V = -\sum_{\substack{I=a,b,c \\ i=1,2,3}} \frac{1}{r_{Ti}} + \frac{1}{2} \sum_{i,j=1}^3 \frac{1}{r_{ij}}$ (for H_3). It can be easily proved that for the new distance $R' = R\gamma^{-1}$ and the new value α' the new

Table 3a. Molecular basis set for H₃ in terms of the orthonormal one-electron orbitals. The numbers assigned to these correspond to those used in Table 1. $|\phi_1 \phi_2 \phi_3| \equiv |\phi_1 \alpha \phi_2 \beta \phi_3 \alpha|$. The order is the same as for the coefficients of Table 5

$$\begin{aligned}
 & |3 \ 1 \ 1| \\
 (2/\sqrt{6}) & |2 \ 3 \ 1| + (1/\sqrt{6}) |3 \ 2 \ 1| + (1/\sqrt{6}) |2 \ 1 \ 3| \\
 -(1/\sqrt{2}) & |3 \ 2 \ 1| + (1/\sqrt{2}) |2 \ 1 \ 3| \\
 & |3 \ 2 \ 2| \\
 (1/\sqrt{3}) & |4 \ 6 \ 1| + (1/\sqrt{12}) |6 \ 4 \ 1| + (1/\sqrt{12}) |4 \ 1 \ 6| + (1/\sqrt{3}) |7 \ 9 \ 1| + (1/\sqrt{12}) |9 \ 7 \ 1| + (1/\sqrt{12}) |7 \ 1 \ 9| \\
 -(1/2) & |6 \ 4 \ 1| + (1/2) |4 \ 1 \ 6| - (1/2) |9 \ 7 \ 1| + (1/2) |7 \ 1 \ 9| \\
 (1/\sqrt{3}) & |5 \ 6 \ 1| + (1/\sqrt{12}) |6 \ 5 \ 1| + (1/\sqrt{12}) |5 \ 1 \ 6| + (1/\sqrt{3}) |8 \ 9 \ 1| + (1/\sqrt{12}) |9 \ 8 \ 1| + (1/\sqrt{12}) |8 \ 1 \ 9| \\
 -(1/2) & |6 \ 5 \ 1| + (1/2) |5 \ 1 \ 6| - (1/2) |9 \ 8 \ 1| + (1/2) |8 \ 1 \ 9| \\
 (1/\sqrt{3}) & |4 \ 6 \ 2| + (1/\sqrt{12}) |6 \ 4 \ 2| + (1/\sqrt{12}) |4 \ 2 \ 6| + (1/\sqrt{3}) |7 \ 9 \ 2| + (1/\sqrt{12}) |9 \ 7 \ 2| + (1/\sqrt{12}) |7 \ 2 \ 9| \\
 -(1/2) & |6 \ 4 \ 2| + (1/2) |4 \ 2 \ 6| - (1/2) |9 \ 7 \ 2| + (1/2) |7 \ 2 \ 9| \\
 (1/\sqrt{3}) & |5 \ 6 \ 2| + (1/\sqrt{12}) |6 \ 5 \ 2| + (1/\sqrt{12}) |5 \ 2 \ 6| + (1/\sqrt{3}) |8 \ 9 \ 2| + (1/\sqrt{12}) |9 \ 8 \ 2| + (1/\sqrt{12}) |8 \ 2 \ 9| \\
 -(1/2) & |6 \ 5 \ 2| + (1/2) |5 \ 2 \ 6| - (1/2) |9 \ 8 \ 2| + (1/2) |8 \ 2 \ 9| \\
 (1/\sqrt{2}) & |3 \ 6 \ 6| + (1/\sqrt{2}) |3 \ 9 \ 9| \\
 (1/\sqrt{2}) & |3 \ 4 \ 4| + (1/\sqrt{2}) |3 \ 7 \ 7| \\
 (1/\sqrt{2}) & |3 \ 5 \ 5| + (1/\sqrt{2}) |3 \ 8 \ 8| \\
 (1/\sqrt{3}) & |4 \ 5 \ 3| + (1/\sqrt{12}) |5 \ 4 \ 3| + (1/\sqrt{12}) |4 \ 3 \ 5| + (1/\sqrt{3}) |7 \ 8 \ 3| + (1/\sqrt{12}) |8 \ 7 \ 3| + (1/\sqrt{12}) |7 \ 3 \ 8| \\
 -(1/2) & |5 \ 4 \ 3| + (1/2) |4 \ 3 \ 5| - (1/2) |8 \ 7 \ 3| + (1/2) |7 \ 3 \ 8| \\
 (2/\sqrt{6}) & |1 \ 3 \ 12| + (1/\sqrt{6}) |3 \ 1 \ 12| + (1/\sqrt{6}) |1 \ 12 \ 3| \\
 -(1/\sqrt{2}) & |3 \ 1 \ 12| + (1/\sqrt{2}) |1 \ 12 \ 3| \\
 (2/\sqrt{6}) & |2 \ 3 \ 12| + (1/\sqrt{6}) |3 \ 2 \ 12| + (1/\sqrt{6}) |2 \ 12 \ 3| \\
 -(1/\sqrt{2}) & |3 \ 2 \ 12| + (1/\sqrt{2}) |2 \ 12 \ 3| \\
 & |3 \ 12 \ 12| \\
 & |10 \ 1 \ 1| \\
 & |11 \ 1 \ 1| \\
 (2/\sqrt{6}) & |2 \ 10 \ 1| + (1/\sqrt{6}) |10 \ 2 \ 1| + (1/\sqrt{6}) |2 \ 1 \ 10| \\
 -(1/\sqrt{2}) & |10 \ 2 \ 1| + (1/\sqrt{2}) |2 \ 1 \ 10| \\
 (2/\sqrt{6}) & |2 \ 11 \ 1| + (1/\sqrt{6}) |11 \ 2 \ 1| + (1/\sqrt{6}) |2 \ 1 \ 11| \\
 -(1/\sqrt{2}) & |11 \ 2 \ 1| + (1/\sqrt{2}) |2 \ 1 \ 11| \\
 & |10 \ 2 \ 2| \\
 & |11 \ 2 \ 2| \\
 (2/\sqrt{6}) & |1 \ 10 \ 12| + (1/\sqrt{6}) |10 \ 1 \ 12| + (1/\sqrt{6}) |1 \ 12 \ 10| \\
 -(1/\sqrt{2}) & |10 \ 1 \ 12| + (1/\sqrt{2}) |1 \ 12 \ 10| \\
 (2/\sqrt{6}) & |1 \ 11 \ 12| + (1/\sqrt{6}) |11 \ 1 \ 12| + (1/\sqrt{6}) |1 \ 12 \ 11| \\
 -(1/\sqrt{2}) & |11 \ 1 \ 12| + (1/\sqrt{2}) |1 \ 12 \ 11| \\
 & |10 \ 12 \ 12| \\
 & |11 \ 12 \ 12| \\
 (2/\sqrt{6}) & |2 \ 10 \ 12| + (1/\sqrt{6}) |10 \ 2 \ 12| + (1/\sqrt{6}) |2 \ 12 \ 10| \\
 -(1/\sqrt{2}) & |10 \ 2 \ 12| + (1/\sqrt{2}) |2 \ 12 \ 10| \\
 (2/\sqrt{6}) & |2 \ 11 \ 12| + (1/\sqrt{6}) |11 \ 2 \ 12| + (1/\sqrt{6}) |2 \ 12 \ 11| \\
 -(1/\sqrt{2}) & |11 \ 2 \ 12| + (1/\sqrt{2}) |2 \ 12 \ 11| \\
 (2/\sqrt{6}) & |10 \ 11 \ 3| + (1/\sqrt{6}) |11 \ 10 \ 3| + (1/\sqrt{6}) |10 \ 3 \ 11| \\
 -(1/\sqrt{2}) & |11 \ 10 \ 3| + (1/\sqrt{2}) |10 \ 3 \ 11| \\
 & |10 \ 3 \ 3| \\
 & |11 \ 3 \ 3| \\
 & |3 \ 10 \ 10| \\
 & |3 \ 11 \ 11| \\
 & |11 \ 10 \ 10| \\
 & |10 \ 11 \ 11| \\
 (1/\sqrt{3}) & |4 \ 6 \ 12| + (1/\sqrt{12}) |6 \ 4 \ 12| + (1/\sqrt{12}) |4 \ 12 \ 6| + (1/\sqrt{3}) |7 \ 9 \ 12| + (1/\sqrt{12}) |9 \ 7 \ 12| + (1/\sqrt{12}) |7 \ 12 \ 9| \\
 -(1/2) & |6 \ 4 \ 12| + (1/2) |4 \ 12 \ 6| - (1/2) |9 \ 7 \ 12| + (1/2) |7 \ 12 \ 9| \\
 (1/\sqrt{3}) & |5 \ 6 \ 12| + (1/\sqrt{12}) |6 \ 5 \ 12| + (1/\sqrt{12}) |5 \ 12 \ 6| + (1/\sqrt{3}) |8 \ 9 \ 12| + (1/\sqrt{12}) |9 \ 8 \ 12| + (1/\sqrt{12}) |8 \ 12 \ 9| \\
 -(1/2) & |6 \ 5 \ 12| + (1/2) |5 \ 12 \ 6| - (1/2) |9 \ 8 \ 12| + (1/2) |8 \ 12 \ 9| \\
 (1/\sqrt{2}) & |10 \ 6 \ 6| + (1/\sqrt{2}) |10 \ 9 \ 9| \\
 (1/\sqrt{2}) & |11 \ 6 \ 6| + (1/\sqrt{2}) |11 \ 9 \ 9|
 \end{aligned}$$

Table 3 (continued)

$(1/\sqrt{2}) 10\ 4\ 4 + (1/\sqrt{2}) 10\ 7\ 7 $
$(1/\sqrt{2}) 10\ 5\ 5 + (1/\sqrt{2}) 10\ 8\ 8 $
$(1/\sqrt{2}) 11\ 4\ 4 + (1/\sqrt{2}) 11\ 7\ 7 $
$(1/\sqrt{2}) 11\ 5\ 5 + (1/\sqrt{2}) 11\ 8\ 8 $
$(1/\sqrt{3}) 4\ 5\ 10 + (1/\sqrt{12}) 5\ 4\ 10 + (1/\sqrt{12}) 4\ 10\ 5 + (1/\sqrt{3}) 7\ 8\ 10 + (1/\sqrt{12}) 8\ 7\ 10 + (1/\sqrt{12}) 7\ 10\ 8 $
$-(1/2) 5\ 4\ 10 + (1/2) 4\ 10\ 5 - (1/2) 8\ 7\ 10 + (1/2) 7\ 10\ 8 $
$(1/\sqrt{3}) 4\ 5\ 11 + (1/\sqrt{12}) 5\ 4\ 11 + (1/\sqrt{12}) 4\ 11\ 5 + (1/\sqrt{3}) 7\ 8\ 11 + (1/\sqrt{12}) 8\ 7\ 11 + (1/\sqrt{12}) 7\ 11\ 8 $
$-(1/2) 5\ 4\ 11 + (1/2) 4\ 11\ 5 - (1/2) 8\ 7\ 11 + (1/2) 7\ 11\ 8 $

Table 3b. *Molecular basis set for H₂ in terms of the orthonormal one-electron orbitals. The numbers also correspond to those of Table 1, and the order is the same as for the coefficients of Table 5 $|\phi_1\phi_2\rangle = |\phi_1\alpha\phi_2\beta\rangle$*

$$\begin{aligned}
 &|1\ 1| \\
 &|2\ 2| \\
 &(1/\sqrt{2})|3\ 3| + (1/\sqrt{2})|5\ 5| \\
 &(1/\sqrt{2})|4\ 4| + (1/\sqrt{2})|6\ 6| \\
 &(1/\sqrt{2})|1\ 8| + (1/\sqrt{2})|8\ 1| \\
 &|8\ 8| \\
 &(1/\sqrt{2})|2\ 7| + (1/\sqrt{2})|7\ 2| \\
 &|7\ 7|
 \end{aligned}$$

Hamiltonian matrix H' is given by:

$$H' = T' + V' = \gamma^2 T + \gamma V. \quad (3)$$

As this new matrix does not depend linearly on the old one, diagonalization must be performed every time. The eigenvector matrix will, therefore, be dependent on α .

From this a set of points on the hypersurface $E(\alpha, \beta, R)$ was obtained. This can be regarded as a variable density medium in a system of co-ordinates (α, β, R) , with density E . A qualitative picture of this is given in Fig. 5, where the vertical shafts cut the (α, β) plane at the values of these parameters considered in the calculation. Then, for each value of (α, β) the value of E was found for 8 fixed distances R . This corresponds to cutting these shafts by horizontal planes $R = R_1, R = R_2, \dots, R = R_8$, and provides a map $E(\alpha, \beta)$ for each value of R , as shown in Fig. 5.

As in most cases, the energy was available only for 4 values of R , for a given value of (α, β) , two optional procedures seemed practicable for the necessary interpolation. One procedure was to fit a parabola to these values by least squares; this would give an estimate of the error as the mean-square deviation. The other was to fit exactly a four-parameter curve. This last procedure was chosen, and a Morse curve was used. This might lead to erroneous results if the values of R were badly distributed, because of the behaviour of a Morse curve. That this did not happen was checked by direct observation of the curves obtained, and further confirmation of the correctness of the procedure was obtained by comparing extrapolated values of R in cases where a large number of points was available. We thus found a deviation of 0.00001 a.u. for reasonably close values of R , and of 0.0004 a.u. for values of R far away. These values will give an upper bound for the mean-square error in these particular cases.

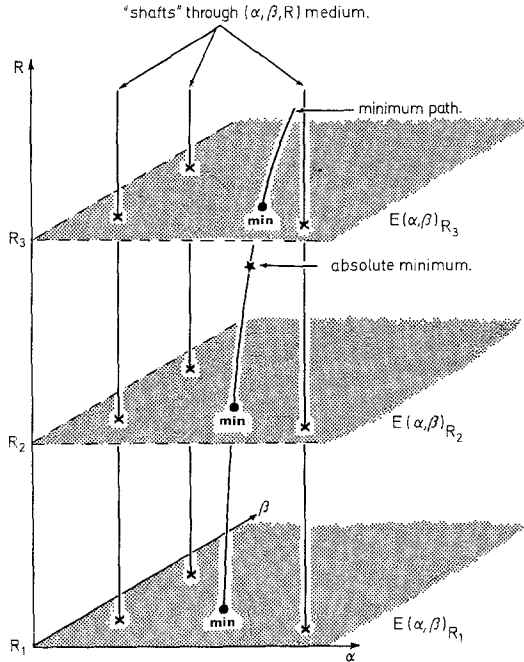


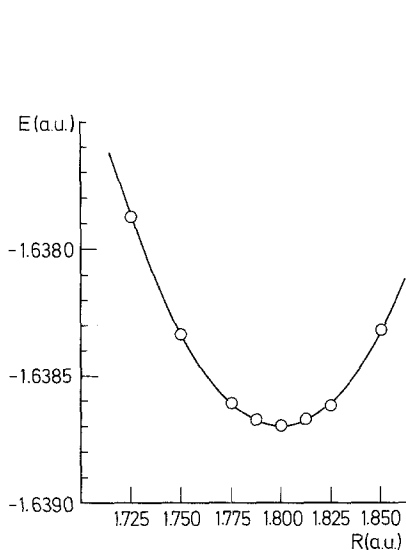
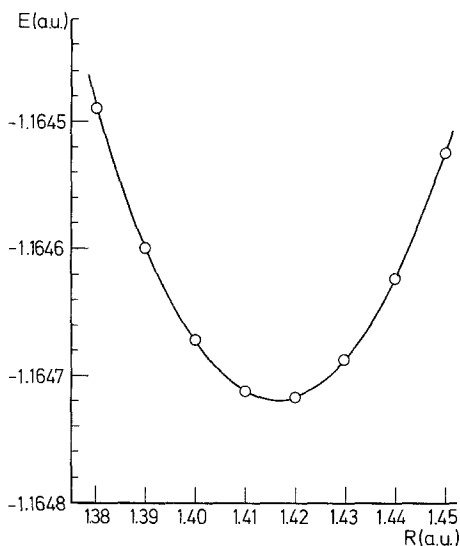
Fig. 5. Qualitative picture of the medium (α, β, R) with point density E . The vertical "shafts" cut the plane (α, β) in points where the value of E is available for several values of R . The planes $R = ct$. cut these shafts in points where the energy is computed by interpolation. This gives the maps $E(\alpha, \beta)$. The minima of these maps are indicated by circles and a star indicates the absolute minimum of the density E in the volume

The line joining the minimum values of E in the maps $E(\alpha, \beta)$ formed in this way will be a minimum path. On it will lie the absolute minimum density of the volume, as shown in Fig. 5. In order to find these minima, the maps were considered as surfaces $E(\alpha, \beta)$, where E is plotted against (α, β) for a fixed R . The surfaces were assumed to join smoothly the points on them for which the value of E was available. An attempt was then made to find the minimum of each surface by means of an analytic approximation using a least-squares fit.

It is interesting to compare the results obtained in the H₃ and H₂ case. In the former, the surfaces present a critical behaviour near the minimum. A set of 29 shafts parallel to the R axis, driven through the volume as described in Fig. 5, was considered to be necessary in order to be able to describe the surfaces accurately in this region. A finite polynomial in α, β involving a reasonable number of parameters did not describe them correctly, and therefore a smooth 14-parameter surface of the form:

$$Z = A + (\exp(-Y) + B \exp(Y)) \sum_{\substack{i=0, 1, 2 \\ j=0, 1, 2, 3}} C_{ij} X^i Y^j \quad (4)$$

was used. A, B and the C_{ij} are the parameters involved, $X = 10(\alpha - 1.21)$, $Y = \beta - 0.875$, $Z = 100(E - 1.6)$, where E is in a.u. These parameters are tabulated in Table 4 for the eight values of R , together with the minimum of each surface.

Fig. 6. Energy for linear, symmetrical H₃Fig. 7. Energy for H₂

The maximum deviation from the 29 known values of the energy was less than 0.00016 a.u. and the maximum mean-square deviation was 0.00005 a.u. The ranges of α and β for this analytic approximation are $1.08 \leq \alpha \leq 1.24$ and $2/3 \leq \beta \leq 5/3$.

In H₂ the situation is rather different. Only 22 shafts were considered necessary, and the behaviour of the surfaces near the minimum is sufficiently regular, so that a simple biquadratic

$$Z = \sum_{\substack{i=0, 1, 2 \\ j=0, 1, 2}} C_{ij} X^i Y^j \quad (5)$$

(where $X = 10(\alpha - 1.19)$, $Y = \beta - 1.5$, $Z = 100(E - 1.16)$, and where E is also in a.u.) would fit the surfaces and give a maximum deviation less than 0.00005 a.u. for the 22 values known, and a maximum mean-square deviation of 0.000026 a.u. The ranges of α and β are in this case $1.18 \leq \alpha \leq 1.22$ and $1 \leq \beta \leq 5/3$. The value of the parameters C_{ij} are also given in Table 4.

In both cases, in order to find the absolute minimum of the volume density on the minimum path, the eight known values of E on it were plotted against the corresponding values of R . As the range is closer than in the Morse interpolation, a parabola was fitted by least-squares to these points. These parabolas obtained for H₃ and H₂ are shown in Figs. 6 and 7, and the values for their minima are -1.6387 a.u. for H₃ at the distance $R = 1.800$ a.u., and -1.1647 a.u. for H₂ at the distance $R = 1.416$ a.u. The maximum deviation for the eight values in this fitting is 0.000014 a.u. for H₃ and 0.000001 a.u. for H₂; the mean-square deviation is 0.000006 a.u. for H₃ and 0.000005 a.u. for H₂. Therefore, as the error in the calculation is estimated to be of the same order as the error of the integrals, i.e. > 0.00001 a.u.,

Table 5. Energy and coefficients of the best ground state wavefunction within the atomic basis set of Table 1, for some values of α , β , R near the optimum ones. The coefficients correspond to the combinations of Slater determinants listed in Table 2

a) H_3 case			
$\alpha = 1.18$ $\beta = 5/6$ $R = 1.771$	$\alpha = 1.18$ $\beta = 5/6$ $R = 1.864$	$\alpha = 1.18$ $\beta = 1$ $R = 1.771$	$\alpha = 1.18$ $\beta = 1$ $R = 1.864$
Energy in a.u.			
-1.63745	-1.63742	-1.63792	-1.63699
Coefficients			
0.841417	0.826377	0.824397	0.807294
0.044555	0.048195	0.044922	0.049716
-0.161376	-0.165572	-0.138268	-0.144443
-0.015306	-0.016357	-0.014728	-0.015674
-0.026238	-0.025923	-0.028394	-0.027857
0.035451	0.034350	0.035947	0.034493
0.004869	0.004665	0.005066	0.004796
0.009178	0.009000	0.008328	0.008175
-0.002306	-0.002270	-0.001614	-0.001580
0.004947	0.004895	0.003837	0.003807
0.001075	0.001105	0.001004	0.001038
0.000718	0.000699	0.000370	0.000364
-0.015674	-0.015973	-0.018017	-0.018276
-0.044757	-0.044992	-0.053134	-0.052742
-0.014373	-0.014619	-0.014520	-0.014910
0.019933	0.020225	0.021294	0.021660
-0.007679	-0.007611	-0.008045	-0.008023
-0.118550	-0.127793	-0.123608	-0.132472
0.417330	0.444260	0.479816	0.504205
-0.040030	-0.045757	-0.041126	-0.047571
0.099826	0.111270	0.098902	0.110946
0.053936	0.063126	0.080948	0.091423
0.185134	0.167630	0.117053	0.097308
0.025919	0.027992	0.033707	0.035500
0.025249	0.025293	0.019334	0.018901
-0.025517	-0.023257	-0.011298	-0.009093
0.010248	0.011191	0.011002	0.011586
-0.012643	-0.015408	-0.012569	-0.013712
-0.005571	-0.005553	-0.003780	-0.003734
-0.000145	-0.000180	-0.000459	-0.000525
-0.041667	-0.041219	-0.023707	-0.021387
0.114807	0.113275	0.095558	0.088377
-0.020767	-0.022068	-0.020269	-0.021609
0.004582	0.008380	0.015989	0.018202
0.017913	0.019512	0.022672	0.023090
-0.005038	-0.004430	-0.001687	-0.001625
-0.018407	-0.019583	-0.013943	-0.014347
0.024223	0.024641	0.015573	0.015061
-0.007811	-0.009629	-0.008318	-0.009335
0.006875	0.009204	0.008630	0.010064
-0.001284	-0.003584	-0.000201	-0.000857

Table 5 (continued)

$\alpha = 1.18$ $\beta = 5/6$ $R = 1.771$	$\alpha = 1.18$ $\beta = 5/6$ $R = 1.864$	$\alpha = 1.18$ $\beta = 1$ $R = 1.771$	$\alpha = 1.18$ $\beta = 1$ $R = 1.864$
Energy in a.u.			
-1.63745	-1.63742	-1.63792	-1.63699
Coefficients			
-0.007323	-0.005857	-0.005916	-0.005489
0.030561	0.030989	0.025047	0.025028
0.012344	0.014773	0.012990	0.013570
-0.030397	-0.029975	-0.025741	-0.025177
-0.007678	-0.008458	-0.007642	-0.008065
0.002060	0.001040	0.000784	0.000528
-0.002989	-0.003023	-0.002189	-0.002128
0.013025	0.013977	0.016298	0.017162
-0.014841	-0.015612	-0.017571	-0.018131
-0.000919	-0.000921	-0.001164	-0.001118
-0.004498	-0.004785	-0.004847	-0.005117
-0.005968	-0.005799	-0.005073	-0.004722
-0.000555	-0.000682	-0.001026	-0.001079
-0.012932	-0.012157	-0.010301	-0.009068
-0.002996	-0.002785	-0.001798	-0.001523
-0.002342	-0.002530	-0.003160	-0.003235
-0.000702	-0.000786	-0.000802	-0.000875
0.003920	0.003623	0.002214	0.001810
-0.000553	-0.000369	-0.000110	-0.000280
0.001094	0.001150	0.001234	0.001330
-0.000463	-0.000458	-0.000401	-0.000423

b) H₂ case

$\alpha = 1.19$ $\beta = 1.5$ $R = 1.412$	$\alpha = 1.19$ $\beta = 1.5$ $R = 1.422$	$\alpha = 1.185$ $\beta = 1.5$ $R = 1.418$
Energy in a.u.		
-1.164733	-1.164705	-1.164732
Coefficients		
0.910262	0.908159	0.910440
-0.016155	-0.016398	-0.016262
-0.064504	-0.064358	-0.064680
-0.012877	-0.012899	-0.012899
-0.391035	-0.395371	-0.390536
0.058025	0.059986	0.057723
0.039280	0.039946	0.039537
-0.094962	-0.095698	-0.095238

an upper bound to the final error in both cases is believed to be 0.0001 a.u., which is quite sufficient for the purposes of this calculation. The value for the force constant of H_3 corresponding to the symmetric mode is 0.296 a.u., in agreement with other calculations [1].

For some values of (α, β, R) near the absolute minimum of the energy in the volume, the value of E is given in Table 5, together with the corresponding coefficients of the basis sets listed in Table 3. The values of (α, β, R) chosen are the same as in Table 1. It can be easily proved that the overlap matrix of the atomic orbitals is independent of the choice of the scaling parameter γ , provided we accordingly vary the distance $R (R' = R\gamma^{-1})$. Hence, the coefficients of the orthonormal sets in terms of the atomic orbital sets, listed in Table 2, will be the same for different values of α , fixed β and the scaled value of R . Therefore only one value of α for every value of β and R is given in Table 2. However, as indicated in the description of the scaling technique, the eigenvector matrix is different for each value of α and therefore the coefficients of Table 5 do depend on this parameter. Nevertheless, for H_3 the optimum value of α was very close to 1.18, so the energy and eigenvectors have only been tabulated for this value. In the next section the conclusions to be drawn from this calculation are discussed.

Conclusion

We have done a full configuration interaction treatment for the linear, symmetrical H_3 system, and thus obtained the best ground state wave function using our 12 basis functions. We have done a similar calculation with the H_2 molecule, using 8 basis functions. We have seen that the variation of the H_2 energy expectation value with the parameters α and β in the atomic basis set is much more regular than in the case of the H_3 system. This must be due to the fact that for H_2 the basis set chosen gives quite a good wave function, using as criterion the proximity of the energy expectation value to the experimental whereas this function is less satisfactory in the case of H_3 . Moreover, we can also point out that a relatively good approximation to the best single determinant is achieved in the case of H_2 by the simple use of a basis set of 1s orbitals. Therefore, one would expect a set of 2p orbitals with a value of the parameter β which would obey some rough criterion to optimize correlation (like minimization of $\int (1s - |2p|)^2 dV$ for 1s and 2p centered on the same atom, which gives $\beta = 5/3$) would give a value of the energy not too far from the minimum one which is obtained here, and this was found to be the case, as can be checked using the analytic approximation (5). However, this is not so in the H_3 case, and a larger set is undoubtedly needed than the 1s one in order to achieve a good approximation to the best single Slater determinant.

Thus it is not surprising that we find a high value for the activation energy of the reaction $H + H_2 = H_2 + H$ of 0.0260 a.u. or 16.3 kcal/mole, compared with the experimental estimate of 7 to 10 kcal/mole [3], as this is given as the difference between two relatively large quantities whose degrees of approximation to the exact ground state energies are different between two relatively large quantities whose degrees of approximation to the exact ground state energies are different, each separate error being much larger than this difference.

Computational Details

The main bulk of the calculation was carried out with the Titan computer in Cambridge. The one-electron and two-electron coulomb integrals were computed by means of C. C. J. Roothaan's standard formulae [4]. The rest of the two-centre integrals were obtained in the Atlas computer at Harwell, using the numerical method by A. C. Switendick and F. J. Corbato [5]. The programs QCPE 22 and 23 were used for the three-centre integrals. A program was then written which assembled the small number of different integrals needed, expanded them into the smallest possible set which took no account of the symmetry of the system, transformed these integrals into the corresponding set for the orthonormal basis, set up from this set the Hamiltonian matrix elements in the molecular representation, and diagonalized this matrix. The transformation of the integrals was checked by back transformation to the original basis set, and for the two-electron case by direct application in a few cases of the direct product transformation (instead of the double transformation used in the program). A further check on the accuracy of the programs was done by using another orthonormal one-electron basis set built from the same AO's.

Acknowledgements. We would like to thank Dr. E. A. G. Armour, Dr. G. Smith and Mr. M. Wakefield for very useful discussions, Mrs. J. Thomas and the staff of the Cambridge University Mathematical Laboratory for computational assistance, and Mr. A. West for furnishing his translation of the QCPE 23 program. A. Riera thanks the British Council for a maintenance grant.

References

1. For example Conroy, H., and D. L. Bruner: *J. chem. Physics* **42**, 4047 (1965); **47**, 921 (1967). — Hirschfelder, J., H. Eyring, and N. Rosen: *J. chem. Physics* **4**, 121 (1936). — Boys, S. F., and I. Shavitt: Technical report WIS-AF-13, Univ. of Wisconsin, Naval Research Laboratory. — Shavitt, I., R. M. Stevens, F. L. Minn, and M. Karplus: *J. chem. Physics* **48**, 2700 (1968) (the present computations were completed before the paper was available to the authors).
2. Eyring, H., J. Walter, and G. E. Kimball: *Quantum chemistry*. New York: J. Wiley & Sons Inc. 1961.
3. Shulz, W. R., and D. J. Le Roy: *J. chem. Physics* **42**, 3869 (1965). — Kupperman, A., and J. M. White: *J. chem. Physics* **44**, 4352 (1966). — Westenberg, A. A., and N. de Haas: *J. chem. Physics* **47**, 1393 (1967). — Le Roy, D. J., B. A. Ridley, and K. A. Quickert: *Discuss. Faraday Soc.* **44**, 92 (1967).
4. Roothaan, C. C. J.: *J. chem. Physics* **19**, 1445 (1951).
5. Switendick, A. C., and F. J. Corbato: *Methods in computational physics*, Vol. 2. New York: Academic Press 1963.

Professor J. W. Linnett
Department of Physical Chemistry
University of Cambridge
Lensfield Road
Cambridge CB2 1EP, England