The Use of Correlated Gaussian Wavefunctions for the Calculation of Chemical Energies for Small Systems

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The purpose of this paper was to investigate the use of limited sets of Gaussian functions as bases to calculate dissociation and activation energies. Gaussian functions have the principal advantage that they lead to integrals that can be performed analytically, even when explicit correlation terms are introduced.

Calculations were performed on H_2 and linear H_3 using a restricted $1s$-type Gaussian basis, and direct correlation factors were introduced into the wave function in both cases. The best result for the dissociation energy of H_2 was 105.1 kcal/mole. However, the activation energy of the hydrogen atom–hydrogen molecule exchange reaction was calculated to be 15.8 kcal/mole.

Die Anwendungsmöglichkeit von Basissätzen einer beschränkten Zahl von Gaußfunktionen zur Berechnung von Dissoziations- und Aktivierungsenergien wird untersucht. Der Hauptvorteil bei der Verwendung von Gaußfunktionen besteht darin, daß sie auf Integrale führen, die analytisch aus-gewertet werden können, sogar im Falle, daß explizite Korrelationsanteile in den Funktionen ent-halten sind.

Für H_2 und lineares H_3 wurde eine eingeschränkte Gaußfunktionenbasis vom $1s$-Typ unter Einschluß expliziter Korrelationsanteile verwendet. Das beste Ergebnis für die Dissoziationsenergie des H_2 beträgt 105,1 kcal/mol. Dagegen ergibt sich für die Aktivierungsenergie der Austauschreaktion Wasserstoffatom–Wasserstoffmolekül ein Wert von 15,8 kcal/mol.

1. Introduction and General Account of Calculations

The calculations in this paper were instigated by the investigation of Reeves [1], who suggested that it was not necessary to achieve high absolute accuracy in calculations in order to estimate energy differences successfully. Reeves' results were extended in this research by using more elaborate wave functions for H_2 and carrying out corresponding calculations for H_3. In this way the validity of this suggestion could be assessed for the calculation of both dissoci- ation energies and activation energies at least for small chemical systems. A set of $1s$-like atomic functions was used as a basis in all calculations.

The wave functions for the H_2 or H_3 system were constructed using the following alternatives:

1. The Form of Basis
a) One or two $1s$-type Gaussians per atomic $1s$-orbital.
b) Spherical or elliptical space functions.
2. The Form of the Complete Wavefunction.
a) Molecular orbital or configuration interaction treatment.
b) Inclusion of explicit correlation terms or uncorrelated function.

Additional constraints appear in the calculations but these are unimportant relative to the above classification. The first calculations employed a basis of single $1s$-type spherical Gaussians on each nuclear centre. Both molecular orbital and limited configuration interaction wave functions were tested and for each type of function explicit correlation was included in further calculations.

An additional set of calculations using spherical Gaussians was carried out, the atomic $1s$ orbitals being approximated by a double rather than a single Gaussian basis. Only configuration interaction wave functions were investigated in this and subsequent calculations. Calculations on H_3 were continued using elliptical Gaussian functions.

At each stage in the calculation sequence, increased accuracy was achieved. The dissociation energy of H_2 was approximated closely. However, the method of using a limited set of Gaussians was not successful for H_3; at least not in terms of the computational effort required. The reasons for this failure are probably complicated and their discussion is deferred until Section 5.

2. The Hamiltonian and Approximations

All calculations were carried out using the Schrödinger spin-free Hamiltonian:

$$H = H_e + V_{ee} + V_{nn}$$

where H_e, V_{ee}, and V_{nn} are respectively the one-electron, two-electron and nuclear repulsion terms. The operators are given in atomic units.

The one-electron Hamiltonian H_e is given by:

$$H_e = -\tfrac{1}{2} \sum_i \nabla_i^2 - \sum_{ij} \frac{Z_j}{|r_i - A'_j|} .$$

The electron coordinates are $\{r_i\}$ and the stationary nuclear coordinates are $\{A'_j\}$ with corresponding charge Z_j. $Z_j = 1$ for all systems considered here.

The two-electron Hamiltonian V_{ee} is given by:

$$V_{ee} = \sum_{i > j} |r_i - r_j|^{-1} .$$

The equation was solved in the Born-Oppenheimer approximation in which the electronic and nuclear wavefunctions are regarded as independent; then the separable internuclear potential terms is:

$$V_{nn} = \sum_{i > j} |A'_i - A'_j|^{-1} Z_i Z_j .$$

Although the equations were solved in the Born-Oppenheimer approximation, no investigation of the validity of this approximation was carried out for the dynamic system H_3.

The trial wavefunctions obeyed neither the nuclear cusp condition nor the interelectron cusp condition. Basically the main object of the work was to examine the extent to which the use of very limited sets of Gaussian functions, which give a poor representation of the behaviour of the wave function near the nuclei and produce poor absolute energies, may be satisfactory for obtaining energy differences.

For all the calculations performed here the energy changes were deduced for changes which did not alter the number of electrons or the number of nuclei. Cancelling of errors is therefore possible. The absence of the inter-electronic cusp condition is of smaller importance.

Although it would have been very interesting to include both nuclear and electronic cusp conditions the improved wavefunctions would have required much longer computations.

3. Types of Wavefunction Used

As indicated in the introduction the types of wavefunction investigated in this paper can be classified firstly according to basis and secondly according to the type of the total space wavefunction. The algebraic form of the correlation function is discussed in the section on bases since the space and correlation functions have similar structure. The way in which the correlation terms are included in the overall wavefunction is discussed in the second section on the form of the total wavefunction.

3.1. Types of Atomic and Gaussian Basis and the Form of the Correlation Functions

3.1.1. Space Basis Functions

The spherical Gaussian functions can be written:

$$G_s(a\underset{\sim}{A}) = \exp(-a(r - \underset{\sim}{A})^2)$$

where a is the exponent and $\underset{\sim}{A}$ the coordinates of the function-centre. The *tilde* indicates a vector. The evaluation of the integrals arising from a basis such as this were first discussed by Boys [2], and summarised, together with an account of the evaluation of the numerical term, by Shavitt [3].

The integrals for correlated terms of the spherical functions were discussed by Boys [4]. Additional techniques for the evaluation of these integrals are given in a paper to be published later.

The space part of the elliptical Gaussians can be written:

$$G_e(\underset{\sim}{a}\underset{\sim}{A}) = \exp(-\sum_{xyz} a_x(x - A_x)^2)$$

where $\{a\}$ are the exponents and $\{A\}$ the function centres.

The matrix formulation of the elliptical integrals was first given by Singer [5]. However, the forms used here are slightly modified to give an overall wavefunction comparable with that obtained using Boys' integrals. The differences required in the integral formulae are indicated in a paper to be published later, together with a method for the factored matrix forms of the integrals for linear systems.

Atomic 1s-type functions $\{\chi\}$ were formed from the Gaussian functions by linear combinations:

$$\chi_i = \sum_j b_{(ij)} G_{(ij)}$$

where the indices are function labels. (ij) is a contracted double index. The relation between atomic and Gaussian sets can be written in matrix notation but many of the matrix elements are zero so this is inconvenient.

Use of molecular orbital wave functions required the transformation of the atomic basis $\{\chi\}$ to a molecular basis $\{\varphi\}$. This transformation can be written:

$$\varphi = C\chi.$$

For H_2, C is the unnormalised orthogonal matrix

$$\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}.$$

For H_3, C is the unnormalised orthogonal matrix

$$\begin{bmatrix} 1 & \lambda & 1 \\ -1 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}.$$

λ is an adjustable parameter. The antibonding orbital does not occur in the ground state and for this reason its coefficient vector is set to zero.

All correlated integrals have the same dimension as the coupled electron function-space and require a double index per electron. Thus the two-electron integrals required a four-dimensional supermatrix transformation and the three-electron integrals required a six-dimensional supermatrix transformation. All matrices were held and transformed in a coded vector. Considerable effort was expended on the problem of labelling the unique Gaussian integrals in vectors in order that they could be recovered, summed and transformed if necessary.

3.1.2. Correlation Functions

The general form of the two-electron correlation function used with both elliptical and spherical space functions is given by:

$$G(r_{ij}) = \exp(-d(r_{ij})^2)$$

where the indices refer to electron labels.

Thus the symmetry of the correlation function is hyperspherical. This particular form of two-electron function weights the least probable configurations and therefore the contribution due to these configurations must be *subtracted* from the uncorrelated structure.

The three-electron correlation functions can be built from component two-electron functions in two distinct ways: either a symmetrical sum or product of the two-electron functions can be formed.

For the sum function:

$$G_{ijk}^s = \sum_\alpha G_\alpha$$

where $\alpha(= ij$ etc.) is the index for all distinct unordered pairs of the indices i, j and k.

For the product function:

$$G^p_{ijk} = \prod_\alpha G_\alpha .$$

After a preliminary investigation for H_3, G^s_{ijk} was chosen as the more effective correlation function. There are good reasons for thinking that a simple restricted correlation function should have this form. The sum and product functions distinguish different structures, the sum function correlating all electron pairs more effectively.

3.2. Structure of the Total Wavefunction

The overall structure of the H_2 and H_3 wave functions was very simple; conventional uncorrelated molecular orbital or configuration interaction wavefunctions were used and combined with correlation terms to produce correlated functions. The configuration interaction functions incorporated all possible linearly independent Slater determinants that could be formed from the atomic (not Gaussian) basis $\{\chi\}$. Since the correlation functions are always symmetric and the space wavefunction are determinants, the overall wavefunction is antisymmetric.

Correlation destroys the orthogonality properties of the overlap matrix. Thus it is necessary to solve an additional set of secular equations to diagonalise the overlap matrix, in order that both the overlap and Hamiltonian matrices should be simultaneously diagonal.

3.2.1. Space Part of the Wavefunctions

3.2.1.1. Molecular Orbital Wavefunctions

For H_2 the wavefunction is written:

$$\Psi_{mo}(H_2) = \left\| \varphi_1(1)\,\alpha(1)\,\varphi_1(2)\,\beta(2) \right\|$$

where φ_1 is the lowest lying (symmetrical) molecular orbital, corresponding to row 1 of the matrix C, of Section 3.1.1.

For H_3 the wavefunction is written:

$$\Psi_{mo}(H_3) = \left\| \varphi_1(1)\,\alpha(1)\,\varphi_2(2)\,\alpha(2)\,\varphi_1(3)\,\beta(3) \right\|$$

where $\{\varphi\}$ is the molecular basis, corresponding to rows 1 and 2 of C, the molecular coefficient matrix.

The Slater determinants are written conventionally as the sequence of diagonal elements between double bars.

3.2.1.2. Configuration Interaction Wavefunctions

The H_2 configuration interaction wavefunction is written as:

$$\Psi_{ci}(H_2) = \sum_\alpha C_\alpha \left\| \chi_i(1)\,\alpha(1)\,\chi_j(2)\,\beta(2) \right\|$$

where the sum is over the contracted double index α corresponding to all i, j pairs that generate distinct Slater determinants. For H_2 there are four such linearly independent determinants. The basis $\{\varphi\}$ may, of course, be used instead of the basis $\{\chi\}$ in the configuration interaction function.

The H_3 configuration interaction wavefunction can be written:

$$\Psi_{ci}(H_3) = \sum_\alpha C_\alpha \|\chi_i(1)\,\alpha(1)\,\chi_j(2)\,\beta(2)\,\chi_k(3)\,\alpha(3)\|$$

where $k \neq i$ for $\{\chi_i : i = 1, 2, 3\}$. A given sequence of indices i, j, k codes a unique α. There are then nine linearly independent Slater determinants.

For both species the configuration interaction functions may be more briefly written as:

$$\Psi_{ci} = \sum_\alpha^N C_\alpha \Delta_\alpha$$

where $N = 4$ for H_2 and $N = 9$ for H_3.

3.2.2. Introduction of the Correlation Terms and Correlated Wavefunctions

As mentioned in Section 3.1.2, the correlation factor weights improbable structures preferentially. Thus the structures must be subtracted from the uncorrelated determinant (mo) or determinants (ci).

The correlated molecular orbital wavefunction may be written for both H_2 and H_3 as:

$$\Psi_{mo} = \sum_{i=1}^2 C_i \Delta_i$$

where

$$\Delta_1 = \Psi_{mo} \quad \text{(for the appropriate species)}$$
$$\Delta_2 = G\,\Psi_{mo}.$$

G is the correlation function, for H_2 or H_3. If C_1 is positive then C_2 is negative because $G(r_{ij})$ is larger the smaller is r_{ij}.

The form of correlated configuration interaction wavefunction closely resembles that of the correlated molecular orbital functions:

$$\Psi_{ci} = \sum_{i=1}^N (C_i \Delta_i + C_{i+N} G \Delta_i).$$

Again $\{C_{i+N}\}$ are negative as they are the coefficients of correlated determinants. Contracting the notation:

$$\Psi_{ci} = \sum_{i=1}^{2N} C_i \Delta_i,$$
$$\Delta_{i+N} = G \Delta_i \quad \text{for } i = 1(1)\,N.$$

$N = 4$ for H_2 and $N = 9$ for H_3, giving respectively 8 and 18 determinants for the complete configuration interaction correlated wavefunction for H_2 and H_3.

The precise types of calculation carried out are indicated in the next section where the particular constraints on the individual calculations are also listed.

4. Results for Calculations for H_2 and Linear H_3

4.1. Reeves' Results for the Hydrogen Atom (Table 1)

Reeves' results [1] for the hydrogen atom are given in Table 1 in order to indicate the scale of absolute accuracy of the calculations reported in this paper. Only when three or more Gaussians are used does the hydrogen atom energy error (1.88 kcal/mole) become comparable with the exchange reaction activation energy (approximately 10 kcal/mole).

In the notation of Section 3.1.1 the hydrogen atom wave function can be written:

$$\Psi_{1s}(\mathrm{H}) = \sum_i b_i G(a_i, 0).$$

Table 1. Summary of Reeves' results for hydrogen atom

Size of Gaussian basis	Exponents a	Linear multipliers b	Energy a.u.	Energy error	
				a.u.	kcal/mole
1	0.2829	0.6515	−0.4244	0.0756	47.5
2	0.2015	0.1760	−0.4858	0.014	8.91
	1.3320	0.2425			
3	0.1433	0.1034	−0.4970	0.003	1.88
	0.6577	0.2164			
	4.2392	0.1575			
Exact	—	—	−0.5000	——	——

4.2. Results and Discussion of Present Calculations on H_2 and Linear H_3

4.2.1. Tables of Results

This section refers to three tables of results: Table 2.1 which lists the data for all calculations performed on H_2 and H_3; Table 2.2 which gives the dissociation energies calculated from the H_2 results of Table 2.1; and Table 2.3 which gives the activation energies calculated from the H_2 and H_3 results of Table 2.1, and the H results in Table 1.

The calculations in Table 2.1 are ordered, where possible, in pairs of corresponding H_2 and H_3 calculations. Calculations 1–7 were made with a basis of "single-Gaussian" $1s$ atomic orbitals. Calculations 8–11 use "double-Gaussian" $1s$ atomic orbitals. In calculations 12 and 13 an elliptical double Gaussian basis was used, there being no corresponding calculations for H_2.

4.2.1.1. Notation for All Tables

The first column of all three tables numbers the calculations and to permit easy cross-reference these numbers correspond in all tables. The second column of Tables 2.2 and 2.3 and the third column of Table 2.1 code the type of

Table 2.1. All calculated results for H_2 and H_3

Calc. No.	System	Type code of calc.	Energy a.u.	Nuclear centres A'	Orbital exponents a	Orbital centres A	Linear multipliers b	Correlation exponent d
1	H_2	MSU1	−0.9808	0	$3.70(-1)$[a]	0	—	—
				1.56	$3.70(-1)$	1.56	—	
2	H_3	MSU1	−1.3844	−1.89	$3.37(-1)$	−1.89	—	—
				0	$3.37(-1)$	0	—	
				1.89	$3.37(-1)$	1.89	—	
3	H_2	MSR1	−0.9986	0	$4.10(-1)$	0	—	$1.03(-1)$
				1.57	$4.10(-1)$	1.57		
4	H_3	MSR1	−1.4156	−1.84	$3.12(-1)$	−1.84	—	$3.80(-1)$
				0	$5.26(-1)$	0	—	
				1.84	$3.12(-1)$	1.84	—	
5	H_2	CSU1	−0.9975	0	$3.72(-1)$	$1.98(-2)$	—	—
				1.59	$3.72(-1)$	1.57	—	
6	H_2	CSR1	−1.0081	0	$4.10(-1)$	0	—	$1.03(-1)$
				1.59	$4.10(-1)$	1.59	—	
7	H_3	CSR1	−1.4285	−1.83	$3.12(-1)$	−1.83	—	$3.97(-1)$
				0	$5.28(-1)$	0	—	
				1.83	$3.12(-1)$	1.83	—	
8	H_2	CSU2	−1.1221	0	$2.58(-1)$	$4.83(-2)$	$2.04(-1)$	—
					1.71	$5.92(-1)$	$3.38(-1)$	
				1.45	$2.58(-1)$	1.41	$2.04(-1)$	
					1.71	1.40	$3.38(-1)$	
9	H_3	CSU2	−1.5767	−1.88	$2.21(-1)$	−1.85	1	—
					1.44	−1.83	1.32	
				0	$3.09(-1)$	0	1	
					1.74	0	1.47	
				1.88	$2.21(-1)$	1.85	1	
					1.44	1.83	1.32	
10	H_2	CSR2	−1.1390	0	$2.68(-1)$	$9.37(-2)$	$1.76(-1)$	$3.68(-1)$
					1.65	$9.39(-2)$	$3.38(-1)$	
				1.44	$2.68(-1)$	1.34	$1.76(-1)$	
					1.65	1.34	$3.38(-1)$	
11	H_3	CSR2	−1.5997	−1.81	$2.36(-1)$	−1.72	1	*[b]
					1.53	−1.71	1.32	
				0	$3.80(-1)$	0	1	
					2.13	0	1.47	
				1.81	$2.36(-1)$	1.72	1	
					1.53	1.71	1.32	
12	H_3	CEU2	−1.5779	−1.85	$2.19(-1)$	0	1	—
					$2.33(-1)$	−1.83		
					1.47	0	1.32	
					1.30	−1.83		
				0	$3.08(-1)$	0	1	
					$3.40(-1)$	0		
					1.74	0	1.47	
					1.75	0		

Table 2.1 (continued)

Calc. No.	System	Type code of calc.	Energy a.u.	Nuclear centres A'	Orbital exponents a	Orbital centres A	Linear multipliers b	Correlation exponent d
12	H_3	CEU2	1.5779	1.85	2.19 (−1)	0	1	
					2.33 (−1)	1.83		
					1.47	0	1.32	
					1.30	1.83		
13	H_3	CER 2	−1.6021	−1.79	2.36 (−1)	0	*	*
					2.36 (−1)	−1.70		
					1.58	0	*	
					1.27	−1.67		
				0	4.10 (−1)	0	*	
					3.80 (−1)	0		
					2.30	0	*	
					2.13	0		
				1.79	2.36 (−1)	0	*	
					2.36 (−1)	1.70		
					1.58	0	*	
					1.27	1.67		

[a] The bracketed numbers are powers of 10.

[b] The asterisk indicates that the data are unavailable, although in all cases the values are not critical.

calculation carried out according to the following scheme:

first letter	$\begin{cases} M & \text{molecular orbital wavefunction} \\ C & \text{configuration interaction wavefunction,} \end{cases}$
second letter	$\begin{cases} S & \text{spherical Gaussian basis} \\ E & \text{elliptical Gaussian basis,} \end{cases}$
third letter	$\begin{cases} R & \text{explicit correlation terms included} \\ U & \text{no explicit correlation terms included,} \end{cases}$
digit	$\begin{cases} 1 & \text{one } 1s \text{ Gaussian per atomic } 1s \text{ orbital} \\ 2 & \text{two } 1s \text{ Gaussians per atomic } 1s \text{ orbital.} \end{cases}$

4.2.1.2. Details and Notes for Table 2.1

Column 5 contains the nuclear centre coordinates. As each nuclear centre is associated with one $1s$ atomic function for single $1s$ Gaussians there is one data set corresponding to each nuclear centre. For double-Gaussian atomic orbitals there are two data sets for each nuclear centre. For elliptical Gaussians each Gaussian function is specified by independent axial (z) and radial (x or y) exponents, and each pair is associated with the corresponding Gaussian orbital centre. The exponents are written in the column order $\begin{pmatrix} x \\ z \end{pmatrix}$. An asterisk in the table indicates that the data are not available. However, in all cases this is not critical.

The details of the different calculations, as identified by the numbers in the first column of Table 2.1, are the following:

1. Nuclear and corresponding orbital centre are equal.

2. Nuclear and corresponding orbital centres are equal; all Gaussian exponents are the same. $\lambda = 1.489$ (see Section 3.1.1) λ is the only adjustable molecular orbital coefficient matrix element in the symmetric linear configuration for H_3.

3. Nuclear and corresponding orbital centres are the same.

4. Nuclear and corresponding orbital centres are the same. $\lambda = 1.721$.

5. No corresponding calculation performed for H_3. Polarised (floated) orbital centres were used.

6. All data are identical with data for calculation 3. Correlation coefficient d optimised.

7. Single unoptimised calculation with data from calculation 4.

8. Fully minimised wavefunction.

9. Fully minimised wavefunction.

10. Fully minimised wavefunction.

11. Apart from d all parameters were optimised.

12. Orbital exponents, centres and nuclear centres optimised.

13. Orbital exponents, centres and nuclear centres optimised.

The calculations 10–13 all illustrated the great computational difficulty of finding a minimum in a non-linear parameter space. All other minimisations were carried out by Ransil's method [6].

4.2.2. Discussion of Results for All Tables 2

The purpose of the initial calculations 1–8 was to investigate the accuracy of energy differences calculated using the minimum possible $1s$-type basis.

For the hydrogen molecule it appears that the calculated dissociation energy is not subject to large errors resulting from the absence of cusps in the wavefunctions. (Energy differences in Table 2.2 are, of course, always calculated using the corresponding basis for the hydrogen atom.) The dissociation energy calculated with type 1 function (one Gaussian function per atom) is 83.2, while that using a single Slater orbital per atom is 80.0 kcal/mole. J. P. Chesick et al. [7] using two Gaussian functions per centre obtained 83.4. Also in the series using configuration interaction calculation 5 and 8 gave 93.3 and 94.5 kcal/mole, while that using single Slater functions gave 92.2 kcal/mole. In both sets the variation is small despite the fact that the Slater functions have a cusp whereas the Gaussian functions do not. The addition of the correlation term improves the calculated dissociation energy by 10.6 kcal/mole for the calculations using a molecular orbital treatment with a single Gaussian function per atom (calc. 3), but when two Gaussians per atom are used the improvement is only 6.6 kcal/mole (calc. 6). When a correlation term is added to the configuration interaction treatment with two Gaussians per centre, the improvement is 11.0 kcal/mole (calc. 10). It is possible that the last calculation allows particularly effectively for electron correlation because it is included both through configuration interaction and in the correlation term as well. This would provide additional flexibility.

Table 2.2. Complete energy results for H_2, including dissociation energy

Calc. No.	Type code of calc.	Absolute energy a.u.	Error in absolute energy	Dissociation energy	Error in dissociation energy
1	MSU 1	−0.9808	0.1938 A 121.6 K	0.1328 A 83.4 K	0.0418 A 26.1 K
3	MSR 1	−0.9986	0.1860 A 116.8 K	0.1498 A 94.0 K	0.0246 A 15.5 K
5	CSU 1	−0.9975	0.1771 A 111.2 K	0.1487 A 93.3 K	0.0259 A 16.1 K
6	CSR 1	−1.0081	0.1665 A 104.5 K	0.1593 A 100.0 K	0.0153 A 9.5 K
8	CSU 2	−1.1221	0.0525 A 32.5 K	0.1605 A 94.5 K	0.0141 A 15.4 K
10	CSR 2	−1.1390	0.0356 A 22.9 K	0.1674 A 105.1 K	0.0072 A 4.4 K
Slater	mo			80.0 K	29.5 K
Slater	ci			92.2 K	17.3 K
Exact	—	−1.1746	—	0.1746 A 109.5 K	—

A = atomic units. — K = kcal/mole.

Table 2.3. Complete energy results for H_3, including activation energy

Calc. No.	Type code of calc.	Energy a.u.	Energy of comparable $H_2 + H$	Activation energy a.u.	Activation energy kcal/mole
2 (1)[a]	MSU 1	−1.3844	−1.4052	0.0208	13.1
4 (3)	MSR 1	−1.4156	−1.4230	0.0074	4.6
7 (6)	CSR 1	−1.4285	−1.4325	0.0040	2.5
9 (8)	CSU 2	−1.5767	−1.6079	0.0312	19.6
11 (10)	CSR 2	−1.5997	−1.6248	0.0251	15.8
12	CEU 2	−1.5779	—	—	—
13	CER 2	−1.6021	—	—	—

[a] The numbers in brackets refer to the corresponding calculations for H_2.

The calculations of the activation energy for the reaction of hydrogen atoms with hydrogen molecules are listed in Table 2.3. Activation energies were obtained using the corresponding H, H_2, and H_3 calculations. The absolute accuracy for H_3 increases in the series 2, 4, 7, 9, and 11, as would be expected. However, the calculated activation energy fluctuates in the same series showing that the cancellation of core errors arising from the absence of cusps at the nuclei is not adequate relative to the small activation energy that is being derived. It is possible that this results from the rather special situation of the central proton in H_3.

The first calculations indicate that, for these, the absolute error is so large in comparison with the quantity being calculated that the space wavefunction is

inadequate to allow an accurate predication of the relatively small chemical energy. A further difference between the results for H_2 and H_3 is demonstrated by the fact that on going from calculation 2 to 4, the introduction of a correlation term actually results in a poorer value for the activation energy. The erratic behaviour of the results for calculations 7, 9, and 11 also demonstrates that the total errors are too large with these functions when interest lies in the calculation of such a small energy.

The use of double Gaussian $1s$ atomic orbitals greatly reduced the effect of the poor space part of the wavefunction near the nuclei. Thus the result of calculation 9 (19 kcal/mole) corresponds well with the result of Bowen and Linnett [8] (22.8 kcal/mole) where comparable exponent variation of a $1s$-type basis was allowed. The last activation energy calculated from 11 (15.8 kcal/mole) is reasonably satisfactory, though disappointing in terms of the computational effort required.

The purpose of the elliptical Gaussian calculations 12 and 13 was to include polarisation effects more successfully than by merely "floating" spherical Gaussians from their associated nuclear centres. However, the results indicate that the incorporation of elliptical symmetry effects a negligible improvement in the H_3 energy, at least with the limited basis used. For this reason no corresponding calculations with H_2 were attempted.

5. The Computations and Computational Times

The number of Gaussian integrals to be evaluated for a correlated function is of the order of $(N)^{2n}$, where N is the size of the basis set and n is the number of electrons. As a result an energy computation for H_3 is about two hundred times more time-consuming than for H_2 (for the double-Gaussian basis). By far the greatest portion of time was used in integral evaluation. For the H_3 calculation using spherical Gaussian functions roughly 52500 integrals had to be evaluated. For H_2 there were only 990 for the corresponding calculation.

All calculations were performed using the Titan Computer in Cambridge (add-time about 5 micro-seconds). A spherical double Gaussian calculation with correlation required about 8 minutes for H_3, and the corresponding elliptical one about 20. The similar H_2 calculations using spherical Gaussian functions took less than 1 minute.

6. General Discussion

There are two kinds of problem involved in the quantum mechanical computation of activation energies. The first is the difficulty of choosing an adequate wavefunction and of deriving the potential energy surface and barrier height from it. However, in addition, there are the theoretical difficulties such as the assumption of the Born-Oppenheimer approximation, the supposition that the process is adiabatic and also uncertainty regarding tunnelling through the barrier. The last might be particularly important in the present case because protons only are involved. It is not, however, the purpose of this paper to discuss

problems of this second kind because they are common to all computations for this system. Moreover, it does seem probable that a good estimate of the activation energy is about 9 kcal/mole.

The idea behind the present calculations was to examine whether the introduction of specific allowance for electron correlation could make it possible to calculate energy changes with reasonable accuracy, even when the basis function was so simple that the absolute value for the energy was bound to be very inaccurate. There was some hope that this might be successful because the dissociation energy of the hydrogen molecule is, as has been pointed out earlier, calculated to be between 80 and 83.5 kcal/mole when a simple molecular orbital treatment is used, whether the basis consists of a single Gaussian, double Gaussian or single Slater orbital on each atom. The error in the absolute energy changes considerably from one of these calculations to another but the calculated energy change does not. The same is true for the configuration interaction calculations.

The absolute energy errors discussed below are shown in Tab. 2.2. For the dissociation energy of hydrogen, calculation 3 (MSR 1) showed that, although the total error was 117, the error in the energy change (dissociation energy) was only 15.5 kcal/mole. For calculation 6 (CSR 1), the corresponding figures were 104 and 9.5; and for calculation 10 (CSR 2) 22.9 and 4.4 kcal/mole. So, for this quantity, the error in the energy change is very much less than the absolute error, though for calculation 10 the ratio of the two errors (4.4/22.9) is rather greater than the ratio of the dissociation energy to the total energy (110/740). Nevertheless, the results do give some satisfaction because electron correlation is involved in the molecule but not in the separated atoms.

The results for the activation energy are not so satisfactory. Calculation 4 (MSR 1) gives 4.6 kcal/mole, calculation 7 (CSR 1) 2.5 and calculation 11 (CSR 2) 15.8. Comparison of calculations 2 and 4, and of 9 and 11, shows that, in both cases, the calculated activation energy is lowered on introducing a correlation term, as would be expected. The actual errors in the energy of activation are no bigger than those for the dissociation energy of H_2, but they are comparable to the energy being calculated.

Therefore, the conclusion of the present work is that this procedure may be useful for the calculation of large energy changes but cannot be expected to be particularly useful for small energy changes. In such cases the absolute accuracy needs to be greater.

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