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Mixed Basis Functions in Molecular Quantum Mechanics

III. The Linear Symmetric H_3 Molecule

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A series of calculations have been carried out for the linear symmetric H_3 molecule using configuration interaction wavefunctions constructed from a mixed set of 1*s* Slater and floating spherical Gaussian functions. The results, although they do not surpass the best CI results reported in the literature, are sufficiently good to encourage further work along these lines.

Es wurde eine Reihe von Rechnungen für das lineare, symmetrische H_3-Molekül durchgeführt, bei denen Wellenfunktionen mit Konfigurations-Wechselwirkung verwendet werden, die aus einem gemischten Satz von 1*s* Slater- und "floating" sphärischen Gauß-Funktionen konstruiert wurden. Obwohl die Resultate die besten CI Ergebnisse, über die in der Literatur berichtet wird, nicht übertreffen, sind sie so gut, daß sie zu weiterer Arbeit nach dieser Methode ermutigen.

Introduction

H_3 is a system of considerable interests to chemists since it is the activated complex of the exchange reaction

$$H + H_2 \rightleftarrows H_2 + H,$$

which is the simplest chemical reaction involving a transition state and as such it ought to be the easiest to investigate theoretically.

Experimental estimates of the activation energy, defined as the energy difference between H_3 and $H_2 + H$, range between 7 and 10 kcal/mole. The recent kinetic experiments of Le Roy and co-workers [1] point to an activation energy of 9.2 kcal/mole, whereas the more direct measurements of Kuppermann and White [2] yield a value of 7.6 ± 0.5 kcal/mole. One of the main difficulties associated with the experimental determination of the classical barrier height is the effect of quantum mechanical tunnelling, making the relationship of barrier height to experimental activation energy very complex. In this paper the term activation energy will be used to mean the classical barrier height.

The first *ab initio* calculation for H_3 was carried out by Hirschfelder, Eyring and Rosen [3], using configuration interaction techniques with a basis of three 1*s* Slater orbitals with identical orbital exponents, one on each nucleus. The estimated activation energy was 25 kcal/mole, the H_2 energy being obtained by the use of a comparable wavefunction, i.e. constructed from two 1*s* STO's. Enlargement of the 1*s* Slater basis by three more 1*s* STO's resulted in an activation energy of 14.8 kcal/mole, this calculation carried out by Boys and Shavitt [4].

The inclusions of $2p$ orbitals in the basis yielded 11 kcal/mole for the activation energy [5], this being the best CI result so far. The lowest activation energy yet calculated was obtained by Contoy and Bruner [6], 7.7 kcal/mole, with error limits estimated to be ± 1.2 kcal/mole, using a correlated wavefunction. The calculated energy of H_3 was -1.6621 ± 0.002 a.u., which, however, is not an upper bound to the true energy. The calculated upper bound is -1.6551 a.u. which results in an upper bound of 12.1 kcal/mole for the activation energy. The best CI calculation using a Gaussian basis has been carried out by Edmiston and Krauss [7], who have obtained an activation energy of 13.5 kcal/mole.

The main obstacles encountered in variational calculations for a system as complex as H_3 are the problem of integral evaluation and the large number of configurations that need to be included in CI expressions, even in the case of moderately sized basis sets. In the work reported here the problem of integrals was made tractable by the use of mixed bases, containing a small number of $1s$ STO's, and floating spherical Gaussian functions. Mixed bases of this type have already been used for H_3 successfully by Riera and Linnett [8]. To avoid the lengthy CI expansions natural orbitals were used to construct the configurations, resulting in compact wavefunctions, quite easy to manage.

It has been established by other workers that the optimum geometry is the linear symmetric one, hence only this geometry was considered in the present work.

Calculations and Results

A series of configuration interaction calculations were carried out for the linear, equidistant system of three interacting hydrogen atoms, in an attempt to obtain a good upper bound to the ground state energy, in the Born-Oppenheimer approximation. The basic computational methods have been outlined elsewhere [9], so here only the construction of 3-electron configuration interaction wavefunctions and the calculation of the Hamiltonian matrix elements will be discussed.

The configurations included in a given wavefunction are constructed from an orthonormal set of symmetry orbitals, each configuration with the symmetry of the ground state of H_3, viz. ${}^2\Sigma_u^+$. The configurations are divided into three types:

$$\left.\begin{aligned} \Phi^1 &= (iij)^1 = |i\bar{i}j| \\ \Phi^2 &= (ijk)^2 = 6^{-1/2}\{-|i\bar{j}k| + |j\bar{i}k| - 2|i\bar{k}j|\} \\ \Phi^3 &= (ijk)^3 = 2^{-1/2}\{|i\bar{j}k| + |j\bar{i}k|\} \end{aligned}\right\}, \tag{1}$$

where $|i\bar{j}k|$ denotes a normalized Slater determinant constructed from the spin orbitals i, j, k; the bar denoting β spin associated with orbital j, opposed to α spin for orbitals i and k.

The total wavefunction is hence written as

$$\Psi = \sum_i C_i \Phi_i^k, \tag{2}$$

where $\{C_i\}$ is a set of coefficients which minimize the total electronic energy, the superscript k denoting the type of the configuration Φ_i.

The matrix elements of the Hamiltonian matrix,

$$H_{ij} = \langle \Phi_i^k | \mathscr{H} | \Phi_j^l \rangle , \tag{3}$$

where $\mathscr{H}$ is the Hamiltonian operator, were evaluated by a modified version of Kotani's method [10]. Let

$$\Phi_i^k = (i_1\, i_2\, i_3)^k$$

and

$$\Phi_j^l = (j_1 j_2 j_3)^l .$$

The matrix elements can then be calculated by the use of the equation

$$H_{ij} = \sum_P \langle i_1(1)\, i_2(2)\, i_3(3) | \mathscr{H} \mathscr{P} | j_1(1) j_2(2) j_3(3) \rangle\, U(P)_{kl} , \tag{4}$$

where $\mathscr{P}$ is the permutation operator acting on the electronic coordinates and $U(P)_{kl}$ is a coefficient which arises as a result of integration over the spin variables.

For each permutation $\boldsymbol{U}(P)$ is a 3×3 matrix corresponding to the three types of configurations. The 2×2 matrix which results if the first column and the first row are omitted is the spin representation matrix, as given by Kotani [10], for the two linearly independent spin eigenfunctions obtained by the Geneological (or Branching Diagram) method. The $\boldsymbol{U}(P)$ matrices are listed in the Appendix.

After the calculation of the energy and the wavefunction the spinless first order density matrix was calculated using the following method. The density matrix we want is given as

$$\gamma(1|1') = 3 \sum_{i,j} C_i C_j^* \int \Phi_i^k \Phi_j^{l*}\, d\tau_2\, d\tau_3\, d\sigma_1\, d\sigma_2\, d\sigma_3 , \tag{5}$$

where integration is to be carried out over all coordinates except the spatial coordinates of electron 1.

After integration the following equation is obtained:

$$\gamma(1|1') = \sum_{i,j} C_i C_j^* \sum_P U(P)_{kl} \sum_{m=1}^{3} i_m(1) j_m(1') \prod_{n \neq m}^{3} \delta_{i_n j_n} . \tag{6}$$

Hence the spinless first order reduced density matrix can be expressed in the form

$$\gamma(1|1') = \sum_{i,j} \gamma_{ij}\, \varphi_i(1)\, \varphi_j^*(1') , \tag{7}$$

where γ_{ij} is the sum of coefficients arising from the summations in Eq. (6).

The matrix γ is then diagonalized, yielding the natural orbitals and their occupation numbers.

Table 1. The orbital bases used in the various H_3 calculations ($1S$ = $1s$-type Slater orbital, G = Spherical Gaussian function)

Calculation Ref.	Number of basis functions	Number of configurations	Orbital basis and exponents
1	6	34	$1S_A = 1S_C = 0.957$, $1S_B = 0.899$, $1S_{A'} = 1S_{C'} = 1.189$, $1S_{B'} = 1.238$
2	8	83	STO basis as for calculation 1 + $G_1 = G_2 = 1.00$
3	8	28	as for calculation 2
4	8	75	as for calculation 2
5	12	32	STO basis as for calculation 1 + $G_1 = G_2 = 1.00$, $G_3 = G_4 = G_5 = G_6 = 0.45$
6	16	43	STO basis as for calculation 1 + $G_1 = G_2 = 1.00$, $G_3 = G_4 = \cdots = G_{10} = 0.45$
7	20	62	STO basis as for calculation 1 + $G_1 = G_2 = 1.00$, $G_3 = G_4 = \cdots = G_{14} = 0.45$
8	20	169	as for calculation 6

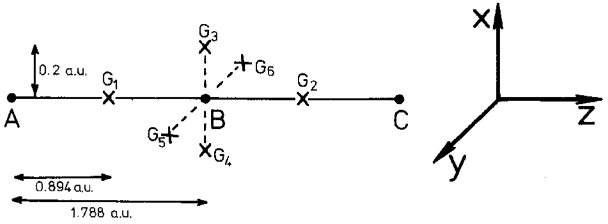

Fig. 1. Positions of the Gaussians in the 8 and 12 orbital H_3 calculations [2–5]

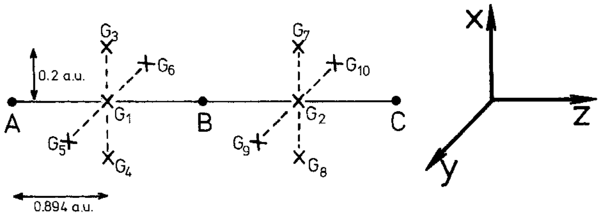

Fig. 2. Positions of the Gaussians in the 16 orbital H_3 calculation [6]

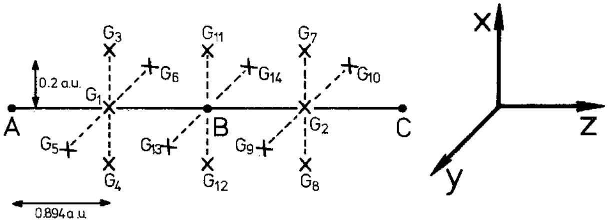

Fig. 3. Positions of the Gaussians in the 20 orbital H_3 calculations [7, 8]

The basis functions used in the various calculations are summarized in Table 1, the spatial arrangement of the Gaussians being shown in Figs. 1–3. The resulting energy terms are presented in Table 2.

Our first calculation is identical to one of Shavitt's [5] H_3 calculations, the STO basis containing six 1*s* type orbitals proved a very convenient starting point, just as in the H_2 calculations [11]. In the subsequent calculations this basis was enlarged by Gaussians only, keeping the internuclear separation constant at 1.788 a.u., this being the optimum distance in calculation Ref. [1].

Calculations Refs. [2, 3, and 4] employ the 6 orbital Slater basis enlarged by two Gaussians, both placed along the molecular axis, halfway between each pair of adjacent nuclei respectively (see Fig. 1). The exponent was chosen as 1.00 on the basis of an analogous H_2 calculation [11] and the results of Riera and Linnett [8]. The first 8 orbital wavefunction was of the full CI type, including all possible configurations, totalling 83, constructed from a Schmidt orthonormalized set of σ_g- and σ_u-type symmetry orbitals. Once the natural orbitals were available the calculation was repeated using the same number of configurations, now built from the NO set. The natural orbitals and their occupation numbers from this calculation are presented in Table 3. In the next calculation Ref. [3] the CI expansion was shortened to include only 28 configurations, those with the highest coefficients from the set of 83. The resultant energy is only 0.16 kcal/mole higher than the energy corresponding to the full CI wavefunction, a numerical illustration of the good convergence properties of natural orbitals. To put the 8 orbital calculations in perspective with similar calculations using STO bases a further calculation Ref. [4] was carried out. From the CI expansion all configurations of the form $(\sigma_u \sigma_u \sigma_u)$ were omitted, leaving 75 $(\sigma_g \sigma_g \sigma_u)$ types. The energy, -1.63415 a.u., is to be compared with the energy -1.6343 a.u., calculated by Gianinetti *et al.* [12], using a 9 orbital basis consisting of 1*s*, 2*s* and $2p_\sigma$ type Slater functions. The two results show the same degree of agreement as the analogous H_2 results [11]. Consequently, significant improvement in the energy seemed unlikely, were the orbital exponents or the positions of the Gaussians allowed to vary. Thus no attempt was made to optimize any non-linear parameters at this stage.

Next the orbital basis was enlarged so as to include functions with angular dependence, i.e. linear combinations of off-axial Gaussians (calculations Refs. [5–8]). The symmetry orbitals formed from these additional Gaussians transform as the irreducible representations of the D_{4h} point group. After the Schmidt orthogonalization of these symmetry orbitals to the σ-type natural orbitals of calculation Ref. [2], CI wavefunctions of various lengths, which, however, always included the 28 basic $(\sigma\sigma\sigma)$ configurations, were constructed and used to calculate the energy. In calculation Ref. [5], 32 configurations were found to contribute significantly to the wavefunction; in calculations Refs. [6] and [7] this number became 43 and 62 respectively. The positions of the off-axial Gaussians were fixed as shown in Figs. 1–3, but their orbital exponents were optimized in calculations Refs. [5] and [6]. Although the orbital basis for calculations Refs. [7] and [8] consisted of 20 functions, the set of orthonormal molecular orbitals which were used for the construction of configurations contained only 16 orbitals, listed in Table 4. Tests showed that the omitted

Table 2. Summary of the results of the various H_3 calculations (all energies given in a.u.) for a constant internuclear separation of 1.788 a.u., together with the resulting activation energies; the energy of H_2 obtained from an "analogous" calculation [11]. Some literature values are also given for comparison purposes

Calculation Ref.	Number of basis functions	Number of configurations	Total energy	Kinetic energy	Nuclear attraction energy	Electron repulsion energy	Energy of dominant configuration	Apparent correlation energy	Activation energy (kcal/mole)	"Analogous" H_2 calculation [11]
1	6	34	−1.63051	1.62994	−5.91530	1.25664	−1.58874	−0.04177	14.01	1
2	8	83	−1.63913	1.63786	−5.93409	1.25888	−1.59247	−0.04666	12.48	2
3	8	28	−1.63885	1.63976	−5.93639	1.25957	−1.59247	−0.04538		
4	8	75	−1.63415	1.63418	−5.93419	1.26765	−1.59247	−0.04168		
5	12	32	−1.64468	1.63901	−5.93216	1.25026	−1.59247	−0.05221		
6	16	43	−1.65075	−1.64120	−5.92818	1.23802	−1.59247	−0.05828	11.26	6
7	20	62	−1.65126	1.64077	−5.92685	1.23661	−1.59247	−0.05879	11.11	8
8	20	169	−1.65170	1.63933	−5.92547	1.23623	−1.59247	−0.05923	10.83	8
1s, 1s′, 2p STO basis, 176 configurations [5]			−1.65207						11.02	
Extensive Gaussian basis, limited CI calculation [7]			−1.6493						13.5	
Correlated wavefunction [6]			−1.6621 ± 0.0002						7.7 ± 1.2	

Table 3. Natural orbitals resulting from the 8 orbital, 83 configuration H_3 calculation, expressed in terms of the original basis, and their occupation numbers

Natural orbital and its symmetry	Occupation number	Coefficient of atomic orbital							
		$1S_A$	$1S_B$	$1S_C$	$1S_{A'}$	$1S_{B'}$	$1S_{C'}$	G_1	G_2
6 σ_g	1.95543	−0.071980	0.222910	−0.071980	0.388138	0.333717	0.388138	0.029482	0.029482
2 σ_u	0.999075	0.843834	0.0	−0.843834	−0.031866	0.0	0.031866	0.028977	−0.028977
4 σ_g	0.034023	0.951084	−1.719274	0.951084	0.200340	−0.019901	0.200340	−0.025052	−0.025052
5 σ_u	0.005327	−3.555260	0.0	3.555260	3.038208	0.0	−3.038208	0.512052	−0.512052
3 σ_g	0.005000	0.103535	3.429927	0.103535	−0.504551	−2.357188	0.504551	−0.419680	−0.419680
8 σ_u	0.000642	4.062570	0.0	−4.062570	−4.448283	0.0	4.448283	1.006045	−1.006045
1 σ_g	0.000433	7.020820	−9.900747	7.020820	−5.314858	7.694885	−5.314858	−0.440515	−0.440515
7 σ_g	0.000057	3.837769	0.444749	3.837769	−4.010764	−2.937294	−4.010764	1.723347	1.723347

Table 4. The orthonormal molecular orbital basis set $\{\varphi_i\}$ used in the 20 orbital H_3 calculations

$\varphi_1, \varphi_2, \ldots, \varphi_6$ are identical to the σ-type natural orbitals 1, 2 ... 6 as listed in Table 3.	
φ_7 is identical to orbital 8 from Table 3.	
$\varphi_8 = 2.18046\,(G_3 - G_4 + G_7 - G_8)$	$e_{1u_x}\,(\pi_{u_x})$
$\varphi_9 = 2.18046\,(G_5 - G_6 + G_9 - G_{10})$	$e_{1u_y}\,(\pi_{u_y})$
$\varphi_{10} = 3.71273\,(G_3 - G_4 - G_7 + G_8)$	$e_{1g_x}\,(\pi_{g_x})$
$\varphi_{11} = 3.71273\,(G_5 - G_6 - G_9 + G_{10})$	$e_{1g_y}\,(\pi_{g_y})$
$\varphi_{12} = 16.2523\,(G_3 + G_4 - G_5 - G_6 + G_7 + G_8 - G_9 - G_{10})$	$b_{1g}\,(\Delta_g)$
$\varphi_{13} = 27.6738\,(G_3 + G_4 - G_5 - G_6 - G_7 - G_8 + G_9 + G_{10})$	$b_{1u}\,(\Delta_u)$
$\varphi_{14} = -8.52780\,(G_3 - G_4 + G_7 - G_8) + 15.1800\,(G_{11} - G_{12})$	$e_{1u_x}\,(\pi_{u_x})$
$\varphi_{15} = -8.52780\,(G_5 - G_6 + G_9 - G_{10}) + 15.1800\,(G_{13} - G_{14})$	$e_{1u_y}\,(\pi_{u_y})$
$\varphi_{16} = 3.83114\,(S_A + S_C) - 4.19685\,S_B - 2.79921\,(S_{A'} + S_{C'})$ $- 2.52582\,S_{B'} - 0.611406\,(G_1 + G_2)$ $+ 1.52691\,(G_{11} + G_{12} + G_{14})$	$a_{1g}\,(\sigma_g)$

Table 5. Occupation numbers of the natural orbitals from the 20 orbital, 62 configuration H_3 calculation

Natural orbital	Occupation number
6 σ_g	1.949173
2 σ_u	0.997099
4 σ_g	0.031928
5 σ_u	0.005044
3 σ_g	0.004892
8 π_{u_x}	0.003876
9 π_{u_y}	0.003876
10 π_{g_x}	0.001386
11 π_{g_y}	0.001386
7 σ_u	0.000544
1 σ_g	0.000339
14 π_{u_x}	0.000137
15 π_{u_y}	0.000137
12 Δ_g	0.000089
13 Δ_u	0.000050
16 σ_g	0.000039

orbitals would make an extremely small contribution to the wavefunction, their absence, however, reduced the computer time and store requirements for the transformation of integrals significantly. The final calculation Ref. [8] was a full CI treatment, using the 16 molecular orbitals of calculation Ref. [7]. The occupation numbers, resulting from the diagonalization of the spinless first order reduced density matrix calculated from the 62 configuration wavefunction, are given in Table 5. The configurations and their coefficients, also from calculation Ref. [7], are listed in Table 6. The wavefunctions resulting from any of the other calculations are given elsewhere [13] [1].

The computational work was performed on the Cambridge University Computer Laboratory's Titan computer, details about which are given elsewhere

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[1] The wavefunctions are available from G. B. Bacskay on request.

Table 6. Configurations and their coefficients, arranged in decreasing order, from the 20 orbital, 62 configuration H_3 calculation

Configuration		Coefficient	Configuration		Coefficient
Orbitals	Type		Orbitals	Type	
6 6 2	1	0.980958	8 10 6	2	0.011278
2 4 6	3	0.121686	9 11 6	2	0.011278
4 4 2	1	−0.073486	1 5 6	3	−0.010954
2 4 6	2	0.067037	2 3 6	2	−0.009617
2 2 5	1	0.040059	1 2 4	3	−0.009531
8 8 2	1	−0.038157	1 1 2	1	−0.008263
9 9 2	1	−0.038157	7 7 2	1	−0.008026
3 5 6	3	−0.034093	10 14 6	3	−0.007432
3 3 2	1	−0.031874	11 15 6	3	−0.007432
8 10 6	3	0.028271	4 5 6	3	0.007096
9 11 6	3	0.028271	2 5 7	2	−0.007028
2 3 6	3	−0.027147	2 2 7	1	−0.005982
5 5 2	1	−0.025171	12 12 2	1	−0.005434
4 5 6	2	−0.024091	14 14 2	1	−0.005234
2 3 4	2	−0.021463	15 15 2	1	−0.005234
2 3 4	3	0.014663	12 13 6	3	0.005232
10 10 2	1	−0.013307	8 10 4	3	0.005028
11 11 2	1	−0.013307	9 11 4	3	0.005028
4 6 7	2	0.012703	3 4 5	2	0.004925
3 5 6	2	−0.012543	10 14 6	2	−0.004377
4 6 7	3	0.012381	3 4 5	3	0.004345
11 15 6	2	−0.004377	8 14 2	3	−0.001552
16 16 2	1	−0.004231	9 15 2	3	−0.001552
1 6 7	3	−0.004189	6 16 2	3	−0.001534
13 13 2	1	−0.003135	8 10 3	3	−0.001504
6 6 5	1	−0.002594	9 11 3	3	−0.001504
8 14 2	2	0.002385	10 10 5	1	−0.001352
9 15 2	2	0.002385	11 11 5	1	−0.001352
4 16 2	3	0.002176	8 14 5	3	−0.001099
12 13 6	2	−0.001713	9 15 5	3	−0.001099
4 16 2	2	−0.001668	6 16 2	2	−0.000951

[9]. In a large calculation, the 16 orbital one for example, the integrals were calculated in several successive runs, the total comp. time required being 50 min. The number of Gaussians used to expand the Slater orbitals for the calculation of 1 and 2 electron integrals were 10 and 8 respectively. For the same calculation transformation of the integrals needed 6 min.; calculation of matrix elements between configurations for a 43 configuration wavefunction 15 sec.; evaluation of the lowest eigenvalue of the Hamilton matrix 6 sec.; calculation of the density matrix, natural orbitals and kinetic and nuclear attraction energies 9 sec.

Discussion

The energy, −1.63913 a.u., resulting from the 8 orbital calculation Ref. [2] is thought to be within 1–2 kcal/mole of the Σ limit for H_3. This belief is based on the results of the analogous H_2 calculation [11], i.e. the 5 orbital one, in which case the calculated energy was ~1.2 kcal/mole above the H_2 Σ limit.

Similarly the SCF energy for H_3, estimated by the energy of the leading term in the natural expansion, viz. -1.59247 a.u., is believed to be accurate to within 1 kcal/mole. (Here, by SCF wavefunction, we mean the best single determinantal function with one doubly filled orbital.) The best SCF energy, corresponding to the same definition of SCF wavefunction, quoted in the literature is -1.592965 a.u., calculated by Edmiston and Krauss [7], using an extensive Gaussian basis. By the addition of two or more Gaussians which could give rise to σ-type symmetry orbitals it should be possible to evaluate both the SCF energy and the Σ limit to an accuracy better than 1 kcal/mole.

The introduction of Gaussian lobe functions with angular dependence resulted in a gradual but considerable lowering of the total H_3 energy. These new functions have greatly improved the correlation part of the wavefunction as evidenced by the decrease in the electron repulsion energy and in the apparent correlation energy. (The latter quantity in calculations Refs. [5–8] was not calculated according to its strict definition, since the dominant configuration in the wavefunction was left unchanged from the 8 orbital calculations. However, the σ-type orbitals constructed from off-axial Gaussians are expected to have only marginal effects on the energy of the dominant configuration.) The close agreement between the two 20 orbital calculations Refs. [7] and [8] is very gratifying and encouraging, giving strong numerical support for the use of natural orbitals. The number of configurations could probably be further reduced if the π and Δ orbitals were transformed to natural basis as well.

The results of the 16 and 20 orbital calculations are to be compared with those of Shavitt *et al.* [5]. The differences are very small, in the case of our 20 orbital, 169 configuration wavefunction only $\sim 1/4$ kcal/mole. Hopefully, by the use of a larger number of Gaussian functions we will be able to find an improved variational upper bound to the H_3 energy that is of "chemical accuracy" (~ 1 kcal/mole). This should not be too difficult a task on the newer, third generation computers.

Unfortunately, we are unable to put forward a new, definitive upper bound for the classical activation energy for the H/H_2 exchange reaction. The values quoted in Table 2 are only meant as a guide since it is very debatable whether the H_2 energies used in the evaluation of activation energies were really resulting from an analogous calculation. Nevertheless, the results that were presented here are promising and the method of mixed basis functions may prove very useful in future work.

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Appendix

The Matrices $U(P)$, *Used in the Evaluation of Matrix Elements between the 3 Electron Configurations*

3 *Electrons*, $S = 1/2$

The three types of configurations with $S = 1/2$ are defined according to Eq. (1). For computational reasons, in case of double occupancy the doubly occupied orbitals are written first, resulting in the following representation matrices $\boldsymbol{U}(P)$:

$$\boldsymbol{U}(1)=\begin{pmatrix} 1 & 0 & \sqrt{2} \\ 0 & 1 & 0 \\ \sqrt{2} & 0 & 1 \end{pmatrix},$$

$$\boldsymbol{U}(12)=\begin{pmatrix} 0 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\boldsymbol{U}(13)=\begin{pmatrix} -1 & \sqrt{3}/\sqrt{2} & -1/\sqrt{2} \\ \sqrt{3}/\sqrt{2} & 1/2 & \sqrt{3}/2 \\ -1/\sqrt{2} & \sqrt{3}/2 & -1/2 \end{pmatrix},$$

$$\boldsymbol{U}(23)=\begin{pmatrix} 0 & -\sqrt{3}/\sqrt{2} & -1/\sqrt{2} \\ -\sqrt{3}/\sqrt{2} & 1/2 & -\sqrt{3}/2 \\ -1/\sqrt{2} & -\sqrt{3}/2 & -1/2 \end{pmatrix},$$

$$\boldsymbol{U}(23.12)=\begin{pmatrix} 0 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{pmatrix},$$

$$\boldsymbol{U}(23.13)=\begin{pmatrix} 0 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix}.$$

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