

Commentationes

Linear Symmetrical H_3 : A CI Function Based on STOs Enlarged with Gaussian Functions

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The wavefunction derived in a previous calculation for the linear symmetrical H_3 system has been improved by the addition of new configurations. These have been constructed from the basis set of Slater orbitals used before, enlarged with a set of five Gaussian functions placed along the internuclear axis. The lowering of the energy calculated was encouraging so that this appears to provide an effective means of enlarging the basis set which does not lead to a great increase in the computational effort.

Die Wellenfunktion, die in einer vorherigen Rechnung über das lineare, symmetrische H_3 -System hergeleitet wurde, ist durch Hinzunahme neuer Konfigurationen verbessert worden. Diese Wellenfunktion wurde mit Hilfe des Basissatzes von Slaterorbitalen, der früher benutzt und um einen Satz von fünf entlang der Kernverbindungsachse plazierten Gaußfunktionen erweitert wurde, konstruiert. Die Erniedrigung der Energie war ermutigend, so daß diese Vergrößerung des Basissatzes eine wirksame Methode zu sein scheint, die nicht zu einem riesigen Anwachsen des numerischen Aufwandes führt.

La fonction d'onde obtenue dans un précédent calcul pour le système linéaire symétrique H_3 a été améliorée par l'addition de nouvelles configurations. Celles-ci ont été construites à partir des orbitales de Slater précédemment utilisées, augmentées de cinq fonctions gaussiennes placées le long des axes internucléaires. L'abaissement d'énergie calculé a été encourageant, ce qui montre une façon d'élargir la base sans trop augmenter l'effort de calcul.

Introduction

In a previous paper [1] a configuration interaction treatment was performed for the linear, symmetrical H_3 system, and the hydrogen molecule. In each case, the one-electron basis set was formed from a set of one "1s" and three "2p" Slater orbitals centered on each nucleus. From the results obtained, it was concluded that this basis set is insufficient, in the case of the H_3 system, to attain a good enough approximation to the observed activation energy.

In a subsequent paper [2] the coefficients of these resulting wavefunctions were transformed into those which correspond to the Slater determinants between the atomic orbitals included in the expansion. The relative importance of the contributions of these determinants was then inferred from a comparison of these coefficients. Their relative magnitudes were discussed, and the results were also compared with those of some other recent calculations on both the

Table 1. Energy and coefficients of the "best" ground state wave functions corresponding to the sixty-two combinations of Slater determinants listed in Table 2 of Ref. [1], for five sets of values of α , β and R

$\alpha = 1.18$ $\beta = 1$ $R = 1.678$	$\alpha = 1.2$ $\beta = 5/6$ $R = 1.742$	$\alpha = 1.18$ $\beta = 1$ $R = 1.771$	$\alpha = 1.2$ $\beta = 5/6$ $R = 1.833$	$\alpha = 1.18$ $\beta = 5/6$ $R = 1.864$
Energy in a.u.				
-1.6351	-1.6377	-1.6379	-1.6379	-1.6374
Coefficients				
0.8412	0.8449	0.8244	0.8298	0.8264
0.0404	0.0422	0.0449	0.0457	0.0482
-0.1323	-0.1604	-0.1383	-0.1646	-0.1656
-0.0138	-0.0147	-0.0147	-0.0157	-0.0164
-0.0288	-0.0264	-0.0284	-0.0261	-0.0259
0.0374	0.0357	0.0359	0.0346	0.0344
0.0053	0.0049	0.0051	0.0047	0.0047
0.0085	0.0091	0.0083	0.0090	0.0090
-0.0016	-0.0024	-0.0016	-0.0024	-0.0023
0.0039	0.0050	0.0038	0.0049	0.0049
0.0010	0.0011	0.0010	0.0011	0.0011
0.0004	0.0007	0.0004	0.0007	0.0007
-0.0177	-0.0157	-0.0180	-0.0160	-0.0160
-0.0534	-0.0450	-0.0531	-0.0453	-0.0450
-0.0141	-0.0143	-0.0145	-0.0146	-0.0146
0.0209	0.0199	0.0213	0.0202	0.0202
-0.0080	-0.0077	-0.0080	-0.0076	-0.0076
-0.1152	-0.1172	-0.1236	-0.1263	-0.1278
0.4530	0.4178	0.4798	0.4445	0.4443
-0.0353	-0.0387	-0.0411	-0.0442	-0.0458
0.0877	0.0980	0.0989	0.1092	0.1113
0.0699	0.0546	0.0809	0.0638	0.0631
0.1352	0.1761	0.1171	0.1596	0.1676
0.0317	0.0196	0.0337	0.0216	0.0280
0.0194	0.0241	0.0193	0.0242	0.0253
-0.0129	-0.0236	-0.0113	-0.0214	-0.0233
0.0104	0.0097	0.0110	0.0105	0.0112
-0.0114	-0.0112	-0.0126	-0.0137	-0.0154
-0.0038	-0.0052	-0.0038	-0.0052	-0.0056
-0.0004	-0.0000	-0.0005	0.0000	-0.0002
-0.0254	-0.0406	-0.0237	-0.0402	-0.0412
0.1000	0.1102	0.0956	0.1087	0.1133
-0.0189	-0.0199	-0.0203	-0.0211	-0.0221
0.0138	0.0017	0.0160	0.0050	0.0084
0.0215	0.0174	0.0227	0.0189	0.0195
-0.0017	-0.0053	-0.0017	-0.0048	-0.0044
-0.0132	-0.0176	-0.0139	-0.0188	-0.0196
0.0155	0.0227	0.0156	0.0231	0.0246
-0.0073	-0.0074	-0.0083	-0.0091	-0.0096
0.0073	0.0060	0.0086	0.0081	0.0092
0.0004	-0.0013	-0.0002	-0.0035	-0.0036
-0.0062	-0.0075	-0.0059	-0.0061	-0.0059
0.0250	0.0313	0.0250	0.0318	0.0310
0.0123	0.0125	0.0130	0.0149	0.0148
-0.0262	-0.0307	-0.0257	-0.0303	-0.0300

Table 1 (continued)

$\alpha = 1.18$	$\alpha = 1.2$	$\alpha = 1.18$	$\alpha = 1.2$	$\alpha = 1.18$
$\beta = 1$	$\beta = 5/6$	$\beta = 1$	$\beta = 5/6$	$\beta = 5/6$
$R = 1.678$	$R = 1.742$	$R = 1.771$	$R = 1.833$	$R = 1.864$
Energy in a.u.				
-1.6351	-1.6377	-1.6379	-1.6379	-1.6374
Coefficients				
-0.0072	-0.0076	-0.0076	-0.0084	-0.0085
0.0010	0.0022	0.0008	0.0013	0.0010
-0.0022	-0.0029	-0.0022	-0.0029	-0.0030
0.0153	0.0130	0.0163	0.0140	0.0140
-0.0169	-0.0149	-0.0176	-0.0156	-0.0156
-0.0012	-0.0009	-0.0012	-0.0009	-0.0009
-0.0046	-0.0045	-0.0048	-0.0047	-0.0048
-0.0053	-0.0058	-0.0051	-0.0057	-0.0058
-0.0010	-0.0005	-0.0010	-0.0006	-0.0007
-0.0114	-0.0125	-0.0103	-0.0118	-0.0122
-0.0020	-0.0028	-0.0018	-0.0026	-0.0028
-0.0031	-0.0020	-0.0032	-0.0022	-0.0025
-0.0007	-0.0006	-0.0008	-0.0007	-0.0008
0.0025	0.0037	0.0022	0.0034	0.0036
-0.0000	-0.0004	-0.0001	-0.0003	-0.0004
0.0011	0.0009	0.0012	0.0010	0.0012
-0.0004	-0.0004	-0.0004	-0.0004	-0.0005

systems. One of the weaknesses of the wavefunctions used in Ref. [1] was derived from the fact that the exponents in the orbitals centered on the middle nucleus were kept the same as those of the corresponding orbitals centered on the outer nuclei.

The conclusions drawn from this examination suggested the addition of a set of five "1s" Gaussian functions to the previous one electron basis set:

$$1g_i = \left(\frac{2\alpha_i}{\pi} \right)^{3/4} \exp(-\alpha_i r_i^2) \quad (1)$$

where $i = a, b, c, d, e$, and where a, b, c stand for the positions of the three protons, as before, and d, e stand for the positions of the mid-points between these protons. The axes conventions are the same as in Ref. [1] (see Fig. 1).

This gives a total of seventeen basis functions and involves five non-linear parameters: α and β in the exponents of the Slater orbitals, and $\alpha_1 = \alpha_a = \alpha_c$, $\alpha_2 = \alpha_d = \alpha_e$, $\alpha_3 = \alpha_b$ in the exponents of the Gaussian functions. It is clear that the general procedure used in Ref. [1], of forming all possible combinations of determinants of symmetry Σ_u^+ which were eigenfunctions of S^2 and S_z belonging to the eigenvalues $S = S_z = \frac{1}{2}$, and using these as the basis for the molecular representation, would now become time-consuming and require a large store. Moreover, there is now the definite advantage that the ground state wavefunction computed in the former calculation is a good approximation to the exact one – although not good enough for obtaining such a relatively small quantity as the

activation energy. This justifies the use of this function as a fixed Ψ_0 , to which further configurations formed from the new one-electron basis set could be variationally added. This was done for five chosen distances. For these, the coefficients of the functions Ψ_0 used, corresponding to the combinations of Slater determinants listed in Table 2 of Ref. [1], are listed in Table 1. These coefficients correspond to the values of the non-linear parameters α and β in the Slater orbitals which gave the nearest energies to the optimum ones of Fig. 6 of Ref. [1].

Calculation

From the set of Gaussian functions (1), the simplest combinations which transform like irreducible representations of the point group $D_{\infty h}$ were constructed. They are:

$$\sigma_s^+ : (1g_a + 1g_c), (1g_d + 1g_e), 1g_b; \quad \sigma_u^+ : (1g_a - 1g_c), (1g_d - 1g_e).$$

These were then made orthogonal to the (orthonormal) one-electron basis set of the previous calculation, and to one another, by a slight modification of the Schmidt method. The resulting coefficients of the new orthonormal set thus obtained, in terms of the atomic orbitals, are given in Table 2, for the five distances considered. Some advantages that this method presented will be mentioned in the last section.

The next stage in this calculation was the construction, from this set of orthonormal orbitals, of the set of Slater determinants which were variationally added to the best computed ψ_0 of the previous calculation. These configurations were obtained by making substitutions in determinants forming ψ_0 , using the new orbitals with the proper symmetry. Combinations of these determinants were then built so as to be eigenfunctions of S^2 and S_z belonging to the eigenvalue $\frac{1}{2}$, besides being of Σ_u^+ symmetry. These combinations are given in Table 3; their choice is explained in the next paragraph.

If ψ_0 were the best single determinantal wavefunction, single substitutions in this function would have no effect, because of Brillouin's theorem. From the conclusions of Ref. [1] the basis set of Slater orbitals which was used to construct ψ_0 is not sufficient for the attainment of a close enough approximation to the best determinant. Therefore, we would like to introduce single substitutions into the best possible determinant using this atomic basis set. However, there is no explicit best determinant in the expansion of ψ_0 . Consequently, we introduced single substitutions in the determinants which form ψ_0 and have relatively large coefficients. Moreover, the introduction of these additional determinants will also increase the correlation of the wavefunction. Only single substitutions were introduced in the present calculation. Configurations formed from double (and triple) substitutions will then introduce further correlation into the wavefunction, and will, therefore, also be important. The use of single substitutions has the additional advantage of reducing the computational effort. Double and triple substitutions will require more effort. Because of this, and because of their large number, the introduction of these configurations will require a careful, more discriminatory analysis than the one carried out in this calculation.

Table 2. Coefficients in expressions for $\psi_1 \dots \psi_{17}$ in terms of $S_A \dots 2p_{x_A} \dots g_a$ etc. for (a) $\alpha = 1.18, \beta = 1, R = 1.678$; (b) $\alpha = 1.2, \beta = 5/6, R = 1.742$; (c) $\alpha = 1.18, \beta = 1, R = 1.771$; (d) $\alpha = 1.2, \beta = 5/6, R = 1.833$; (e) $\alpha = 1.118, \beta = 5/6, R = 1.864$ (see Ref. [1] and [2]).

In 1, 2, 12, 13, 14 and 15, $S_A = S_c, 2p_{z_A} = -2p_{z_c}, g_a = g_c$ and $g_d = g_e$
 In 3, 10, 11, 16 and 17, $S_A = -S_c, 2p_{z_A} = 2p_{z_c}, g_a = -g_c$ and $g_d = -g_e$
 In 4 and 5, $2p_{x_A} = 2p_{x_c}$, and in 6, $2p_{x_A} = -2p_{x_c}$

		(a) $\alpha = 1.18$	$\beta = 1$	$R = 1.678$		
		(b) $\alpha = 1.2$	$\beta = 5/6$	$R = 1.742$		
		(c) $\alpha = 1.18$	$\beta = 1$	$R = 1.771$		
		(d) $\alpha = 1.2$	$\beta = 5/6$	$R = 1.833$		
		(e) $\alpha = 1.18$	$\beta = 5/6$	$R = 1.864$		
		$S_A, (\pm S_c)$	S_B	$2p_{z_A}, (\pm 2p_{z_c})$	$2p_{z_B}$	
1.	(a)	0.2915	0.2282	0.3212	0	
	(b)	0.2957	0.2275	0.3224	0	
	(c)	0.2847	0.2314	0.3329	0	
	(d)-(e)	0.2873	0.2294	0.3346	0	
2.	(a)	-1.0394	2.5625	-0.8768	0	
	(b)	-0.8473	2.2388	-0.8024	0	
	(c)	-0.9523	2.3970	-0.8520	0	
	(d)-(e)	-0.7831	2.1256	-0.7848	0	
3.	(a)	0.4058	0	-0.2769	-0.3018	
	(b)	0.3728	0	-0.2952	-0.2891	
	(c)	0.4247	0	-0.2577	-0.3061	
	(d)-(e)	0.3904	0	-0.2808	-0.2937	
10.	(a)	0.3328	0	0.9250	-0.4012	
	(b)	0.5283	0	0.9474	-0.2859	
	(c)	0.2714	0	0.8974	-0.3791	
	(d)-(e)	0.4576	0	0.9367	-0.2872	
11.	(a)	2.1912	0	0.3503	2.6252	
	(b)	1.6876	0	-0.2174	2.3980	
	(c)	2.0725	0	0.4336	2.5102	
	(d)-(e)	1.6323	0	-0.1021	2.2677	
12.	(a)	-0.5457	-0.0418	0.5248	0	
	(b)	-0.5759	-0.0229	0.5444	0	
	(c)	-0.5539	-0.0415	0.5025	0	
	(d)-(e)	-0.5829	-0.0239	0.5169	0	
		$2p_{x_A}, (2p_{y_A}),$		$2p_{x_B} (2p_{y_B})$		
		$(\pm 2p_{x_c}), (\pm 2p_{y_c})$				
4(7).	(a)	0.4685	0.2730			
	(b)	0.4555	0.2627			
	(c)	0.4749	0.2772			
	(d)-(e)	0.4604	0.2668			
5(8).	(a)	-1.1702	2.0086			
	(b)	-1.3893	2.4087			
	(c)	-1.0909	1.8687			
	(d)-(e)	-1.2959	2.2362			
6(9).	(a)	0.8410	0			
	(b)	0.8931	0			
	(c)	0.8224	0			
	(d)-(e)	0.8709	0			

Table 2 (continued)

		$S_A, (\pm S_c)$	S_B	$2p_{z_A}, (\pm 2p_{z_c})$	$2p_{z_B}$	$g_a, (\pm g_c)$	$g_d, (\pm g_e)$	g_b
13.	(a)	-2.5761	0.1493	-0.0018	0	2.7447	0	0
	(b)	-2.5490	0.2590	0.0079	0	2.6629	0	0
	(c)	-2.5673	0.3914	-0.0572	0	2.6393	0	0
	(d)	-2.6261	0.3308	-0.0080	0	2.7077	0	0
	(e)	-2.5444	0.4250	-0.0323	0	2.5957	0	0
14.	(a)	1.4808	-1.8586	-0.1708	0	-1.8127	1.6006	0
	(b)	1.7141	-2.3103	-0.0241	0	-2.0044	1.7054	0
	(c)	1.6970	-2.1830	-0.2059	0	-2.1255	1.8321	0
	(d)	1.6449	-2.1658	-0.0521	0	-1.9730	1.6757	0
	(e)	1.7084	-2.2245	-0.0263	0	-2.0006	1.6628	0
15.	(a)	-4.9139	-4.7126	-1.1021	0	2.0551	2.3775	7.1810
	(b)	-5.0484	-3.0069	-0.7930	0	2.8663	1.6156	5.4690
	(c)	-4.9350	-4.1206	-1.1273	0	2.1523	2.2706	6.5551
	(d)	-4.7898	-2.4284	-0.7582	0	2.8234	1.3656	4.8432
	(e)	-5.0961	-2.3602	-0.8857	0	2.9814	1.2926	5.2982
16.	(a)	-0.9296	0	-1.1349	1.1449	0	1.8490	0
	(b)	-0.7950	0	-1.0509	1.1311	0	1.6145	0
	(c)	-0.9038	0	-1.1290	1.2471	0	1.9745	0
	(d)	-0.6922	0	-0.9858	1.1012	0	1.5520	0
	(e)	-0.6507	0	-0.9552	1.0684	0	1.4904	0
17.	(a)	-4.4058	0	-0.4822	-0.3126	3.8662	-0.1905	0
	(b)	-4.9861	0	-0.4896	-0.7853	4.2241	-0.3561	0
	(c)	-4.5284	0	-0.4073	-0.8441	3.9117	-0.5098	0
	(d)	-4.9230	0	-0.4493	-0.8698	4.2096	-0.3924	0
	(e)	-5.1759	0	-0.4810	-1.1319	4.2892	-0.4348	0

As in the previous calculation, the Hamiltonian matrix was set up in the representation chosen, and diagonalized by the Jacobi method. The importance of the variation of the non-linear parameters $\alpha_1 = \alpha_a = \alpha_c$, $\alpha_2 = \alpha_d = \alpha_e$; $\alpha_3 = \alpha_b$ in the Gaussian orbitals (1) was also studied. The scaling technique used in Ref. [1] was not useful in this case, because the parameters α and β in the Slater orbitals, and the nuclear configuration had to be kept fixed during each calculation. As the computation of the necessary integrals no longer presented the difficulties encountered in Ref. [1], a more straight-forward method could be used.

The energy was also considered as a "density" function defined in parameter space of co-ordinates $\alpha_1, \alpha_2, \alpha_3$. In order to find the absolute minimum of this "density" a stepwise iteration method would have been too slow, if the variation of the "density" near this minimum was as small as expected. A faster procedure would then be a method of descent. This would, however, involve a prohibitive amount of computation. A simple approximation to it which was found to be satisfactory was made by considering each starting point as the orthocentre of a regular tetrahedron, and using the differences in the density from this point to the vertices, in order to find a path of descent. About two to four cycles of this procedure (with three to four steps along the "descent" path) gave the minimum

Table 3. Combinations of Slater determinants built from the basis set ψ_i defined in Table 2

		12 12 16					
		12 12 17					
		(2/√6) 11 1 13	+	(1/√6) 11 13 1	+	(1/√6) 1 11 13	
		(1/√2) 11 13 1	-	(1/√2) 1 11 13			
5.		(2/√6) 11 1 14	+	(1/√6) 11 14 1	+	(1/√6) 1 11 14	
		(1/√2) 11 14 1	-	(1/√2) 1 11 14			
		(2/√6) 11 1 15	+	(1/√6) 11 15 1	+	(1/√6) 1 11 15	
		(1/√2) 11 15 1	-	(1/√2) 1 11 15			
		1 1 16					
10.		1 1 17					
		(2/√6) 3 1 13	+	(1/√6) 3 13 1	+	(1/√6) 1 3 13	
		(1/√2) 3 13 1	-	(1/√2) 1 3 13			
		(2/√6) 3 1 14	+	(1/√6) 3 14 1	+	(1/√6) 1 3 14	
		(1/√2) 3 14 1	-	(1/√2) 1 3 14			
15.		(2/√6) 3 1 15	+	(1/√6) 3 15 1	+	(1/√6) 1 3 15	
		(1/√2) 3 15 1	-	(1/√2) 1 3 15			
		(2/√6) 2 1 16	+	(1/√6) 2 16 1	+	(1/√6) 1 2 16	
		(1/√2) 2 16 1	-	(1/√2) 1 2 16			
		(2/√6) 2 1 17	+	(1/√6) 2 17 1	+	(1/√6) 1 2 17	
20.		(1/√2) 2 17 1	-	(1/√2) 1 2 17			
		(2/√6) 3 2 13	+	(1/√6) 3 13 2	+	(1/√6) 2 3 13	
		(1/√2) 3 13 2	-	(1/√2) 2 3 13			
		(2/√6) 3 2 14	+	(1/√6) 3 14 2	+	(1/√6) 2 3 14	
		(1/√2) 3 14 2	-	(1/√2) 2 3 14			
25.		(2/√6) 3 2 15	+	(1/√6) 3 15 2	+	(1/√6) 2 3 15	
		(1/√2) 3 15 2	-	(1/√2) 2 3 15			
		(2/√6) 12 1 16	+	(1/√6) 12 16 1	+	(1/√6) 1 12 16	
		(1/√2) 12 16 1	-	(1/√2) 1 12 16			
		(2/√6) 12 1 17	+	(1/√6) 12 17 1	+	(1/√6) 1 12 17	
30.		(1/√2) 12 17 1	-	(1/√2) 1 12 17			
		(2/√6) 3 12 13	+	(1/√6) 3 13 12	+	(1/√6) 12 3 13	
		(1/√2) 3 13 12	-	(1/√2) 12 3 13			
		(2/√6) 3 12 14	+	(1/√6) 3 14 12	+	(1/√6) 12 3 14	
		(1/√2) 3 14 12	-	(1/√2) 12 3 14			
35.		(2/√6) 3 12 15	+	(1/√6) 3 15 12	+	(1/√6) 12 3 15	
		(1/√2) 3 15 12	-	(1/√2) 12 3 15			
		(2/√6) 2 12 16	+	(1/√6) 2 16 12	+	(1/√6) 12 2 16	
		(1/√2) 2 16 12	-	(1/√2) 12 2 16			
		(2/√6) 2 12 17	+	(1/√6) 2 17 12	+	(1/√6) 12 2 17	
40.		(1/√2) 2 17 12	-	(1/√2) 12 2 17			
		(2/√6) 10 1 13	+	(1/√6) 10 13 1	+	(1/√6) 1 10 13	
		(1/√2) 10 13 1	-	(1/√2) 1 10 13			
		(2/√6) 10 1 14	+	(1/√6) 10 14 1	+	(1/√6) 1 10 14	
		(1/√2) 10 14 1	-	(1/√2) 1 10 14			

Table 3 (continued)

45.	$(2/\sqrt{6})$		10	1	15		$+(1/\sqrt{6})$		10	15	1		$+(1/\sqrt{6})$		1	10	15		
	$(1/\sqrt{2})$		10	15	1		$-(1/\sqrt{2})$		1	10	15								
	$(2/\sqrt{6})$		10	12	13		$+(1/\sqrt{6})$		10	13	12		$+(1/\sqrt{6})$		12	10	13		
	$(1/\sqrt{2})$		10	13	12		$-(1/\sqrt{2})$		12	10	13								
50.	$(2/\sqrt{6})$		10	12	14		$+(1/\sqrt{6})$		10	14	12		$+(1/\sqrt{6})$		12	10	14		
	$(1/\sqrt{2})$		10	14	12		$-(1/\sqrt{2})$		12	10	14								
	$(2/\sqrt{6})$		10	12	15		$+(1/\sqrt{6})$		10	15	12		$+(1/\sqrt{6})$		12	10	15		
	$(1/\sqrt{2})$		10	15	12		$-(1/\sqrt{2})$		12	10	15								

with an estimated accuracy of 0.000005 a.u., which is sufficient for our purposes. For the first of the five distances, a smaller basis set was used for the first iterations, until the variation in the density was small enough. For the other distances, the initial values of the parameters were modified according to the values found for the previous distances.

The resulting energies, and the coefficients for the functions Ψ_0 used – which correspond to those of Table 1 – and of the new basis set of Table 3, are tabulated in Table 4. The total error of the calculations is believed to be of the same order as in the previous calculation, i.e., less than 0.0001 a.u.

Conclusion

In this calculation, we have tried to remedy some of the defects found in the wavefunction computed in Ref. [1] for the H_3 system. We have taken the five wavefunctions whose coefficients are given in Table 1, for the five corresponding distances. These functions gave the energies nearest to the best possible ones obtainable using the basis set of Slater orbitals. These functions were then improved according to the present scheme. The basis set of Slater orbitals was enlarged with a set of five Gaussian functions placed along the internuclear axis, and configurations formed from these were chosen, as indicated in the previous section.

The lowest of the energies thus obtained is -1.6438 a.u., for the distance $R = 1.771$ a.u. This represents an improvement of 3.7 Kcal/mole over the energy of the function ψ_0 used for this distance. None of the ψ_0 chosen corresponds to the best energy interpolated from the results of the previous treatment [1]. A parabolic fit was not appropriate for the five values of the energy obtained in this treatment, which were given in Table 4. If we compare the best energy calculated in the first treatment with the lowest energy obtained in this paper – which is quoted above – the improvement is of 3.2 Kcal/mole.

This lowest energy is still greater than that of some of the more detailed calculations already surveyed [2]. Nevertheless, if we take into account the effort involved – which was much less than in the previous calculation – the results are encouraging. Also, it was interesting to examine the use of a mixed set of Slater and Gaussian orbitals as a means of enlarging a basis set without the integration becoming very time-consuming – which would be the case if further Slater orbitals formed from higher polynomials in r , x , y , and z were added.

Table 4. Energy and coefficients for ψ_0 in terms of the fifty-two combinations of Slater determinants listed in Table 3. The five columns correspond to the five sets of values of α and β listed in Table 2

$\alpha = 1.18$ $\beta = 1$ $R = 1.678$	$\alpha = 1.2$ $\beta = 5/6$ $R = 1.742$	$\alpha = 1.18$ $\beta = 1$ $R = 1.771$	$\alpha = 1.2$ $\beta = 5/6$ $R = 1.833$	$\alpha = 1.18$ $\beta = 5/6$ $R = 1.864$
Energy in a.u.				
-1.6424	-1.6433	-1.6438	-1.6431	-1.6425
Coefficients				
0.9979	0.9985	0.9984	0.9984	0.9986
-0.0013	-0.0020	-0.0010	-0.0025	-0.0027
0.0012	0.0006	0.0012	0.0003	0.0003
-0.0022	-0.0035	-0.0026	-0.0038	-0.0036
-0.0067	-0.0060	-0.0072	-0.0065	-0.0069
-0.0028	-0.0030	-0.0027	-0.0033	-0.0029
-0.0051	-0.0021	-0.0040	-0.0016	-0.0012
0.0005	0.0012	0.0007	0.0018	0.0017
0.0054	0.0047	0.0055	0.0057	0.0057
0.0065	0.0004	0.0092	0.0030	0.0018
0.0074	-0.0002	0.0051	-0.0005	-0.0006
0.0288	0.0142	0.0203	0.0036	0.0118
-0.0168	-0.0208	-0.0238	-0.0277	-0.0236
0.0298	0.0178	0.0184	0.0109	0.0146
0.0006	0.0022	-0.0039	-0.0020	0.0009
-0.0113	0.0001	-0.0049	0.0076	0.0016
0.0037	0.0079	0.0080	0.0127	0.0089
0.0058	0.0066	0.0062	0.0054	0.0054
-0.0011	-0.0024	-0.0011	-0.0022	-0.0020
0.0009	-0.0002	0.0005	-0.0007	-0.0006
-0.0002	0.0005	0.0002	0.0009	0.0007
-0.0004	-0.0050	-0.0017	-0.0067	-0.0057
-0.0052	-0.0066	-0.0062	-0.0076	-0.0075
-0.0017	-0.0041	-0.0024	-0.0045	-0.0033
-0.0031	-0.0025	-0.0030	-0.0026	-0.0021
0.0015	0.0046	0.0025	0.0063	0.0051
0.0027	0.0035	0.0033	0.0040	0.0036
-0.0009	0.0029	-0.0023	0.0021	0.0030
-0.0007	-0.0027	0.0001	-0.0030	-0.0033
-0.0013	0.0016	-0.0006	0.0023	0.0022
0.0052	0.0034	0.0049	0.0031	0.0029
-0.0154	-0.0096	-0.0140	-0.0071	-0.0098
-0.0016	0.0016	0.0016	0.0054	0.0029
-0.0197	-0.0131	-0.0164	-0.0114	-0.0120
-0.0109	-0.0083	-0.0082	-0.0064	-0.0075
0.0073	0.0039	0.0058	0.0024	0.0040
0.0027	0.0005	0.0008	-0.0016	0.0003
-0.0027	-0.0024	-0.0031	-0.0021	-0.0021
0.0005	0.0012	0.0006	0.0009	0.0007
-0.0006	-0.0001	-0.0004	0.0003	0.0003
-0.0002	-0.0007	-0.0004	-0.0009	-0.0008
-0.0009	-0.0053	-0.0026	-0.0072	-0.0055
-0.0204	-0.0267	-0.0215	-0.0261	-0.0260
-0.0012	-0.0031	-0.0025	-0.0036	-0.0021
-0.0164	-0.0152	-0.0148	-0.0154	-0.0138

Table 4 (continued)

$\alpha = 1.18$	$\alpha = 1.2$	$\alpha = 1.18$	$\alpha = 1.2$	$\alpha = 1.18$
$\beta = 1$	$\beta = 5/6$	$\beta = 1$	$\beta = 5/6$	$\beta = 5/6$
$R = 1.678$	$R = 1.742$	$R = 1.771$	$R = 1.833$	$R = 1.864$
Energy in a.u.				
-1.6424	-1.6433	-1.6438	-1.6431	-1.6425
Coefficients				
0.0013	0.0048	0.0023	0.0054	0.0039
0.0079	0.0111	0.0083	0.0126	0.0115
-0.0014	0.0007	-0.0007	0.0016	0.0008
0.0086	0.0107	0.0103	0.0119	0.0116
-0.0023	-0.0013	-0.0014	-0.0010	-0.0015
0.0065	0.0055	0.0068	0.0064	0.0056
0.0004	-0.0008	-0.0001	-0.0008	-0.0003
-0.0029	-0.0041	-0.0036	-0.0053	-0.0046

As in the previous calculation, the coefficients of the resulting wavefunctions were transformed into those which correspond to ψ_0 and to the Slater determinants between the atomic orbitals. These included determinants which involved Gaussian orbitals, but also determinants involving only Slater orbitals. Because of this, and because of the increasing complexity of the wavefunction, it was found very difficult to interpret its form. The most important determinants were those which involve the Gaussian orbital centered on the middle nucleus. These probably partially compensate the weakness in the previous calculation which was mentioned in the first section. Most of the determinants have very small coefficients, and it is quite possible that some of them can be neglected with a minimal change in the energy; this would be of importance if the molecular basis set is further enlarged.

Appendix

Computational Details

The whole of this calculation was carried out with the Titan computer in Cambridge. The integration method used was a Gaussian expansion for the Slater orbitals. For this, the coefficients given by Huzinaga *et al.* [3] were used. The general formulae given there were applied to the special cases of $1s$ and $2p$ functions. The integrals between Gaussian orbitals were then obtained in terms of the auxiliary function defined in Ref. [3], and the one-dimensional integral

$$F_m(t) = \int_0^1 u^{2m} e^{-tu^2} du \quad (t > 0) \quad (2)$$

where m is at most equal to two for a nuclear attraction integral, and at most four for an electron repulsion integral between $1s$ and $2p$ Gaussian orbitals. In order to have an estimate of the error in its evaluation, the asymptotic expansion

given by Shavitt [4] for the complementary function of $F_m(t)$:

$$\Phi_m(t) = \int_1^\infty u^{2m} e^{-tu^2} du = F_m(t) + \frac{\Gamma(m + \frac{1}{2})}{2t^{m + \frac{1}{2}}} \tag{3}$$

was used. An upper bound to the error in Φ_m is given by the first term after truncation in the expansion:

$$\Phi_m(t) = \frac{e^{-t}}{2t} \left(1 + \frac{2m-1}{2t} + \frac{(2m-1)(2m-3)}{(2t)^2} + \dots \right). \tag{4}$$

This gives an upper bound from (3) to the corresponding error in $F_m(t)$. This asymptotic expansion was used for small intervals of t , for a wide range of this variable. The series was truncated whenever the error bound computed from the next term to be added was less than 10^{-8} , or when the terms began to increase. This last case was considered a failure for this method to be used for comparison purposes. From this, it was found to be useful for values of $t \geq 8$. For $0 < t < 8$, the method used to obtain an estimate of the errors was chosen to be the successive differentiation of the Chebyshev expansion for $F_0(t)$. This was obtained from the corresponding expansion for $\text{erf}(x)$ given by Clenshaw [5]:

$$F_0(t) = \frac{1}{2} \sqrt{\frac{\pi}{t}} \text{erf}(\sqrt{t}) = \frac{\sqrt{\pi}}{8} \Sigma'_s a_{2s} T_{2s} \left(\frac{\sqrt{t}}{4} \right) = \Sigma'_s a_s^{(0)} T_s \left(\frac{1}{8} t - 1 \right) \tag{5}$$

for $0 \leq t \leq 16$, where $a_s^{(0)} = \frac{\sqrt{\pi}}{8} a_{2s}$. Although single length arithmetic (11 digits) was used throughout, and the differentiation of a truncated power series can be very unreliable, the procedure was seen to be valid for the accuracy required for m up to ten (all the methods were written for these values), by comparison with the asymptotic expansion (4), for the range $t = 8$ to $t = 16$. As the amplitudes of the error oscillations of the truncated Chebyshev expansions are practically constant throughout their range of validity [6], this method was considered acceptable for the range $t = 0$ to $t = 8$.

Finally, we used the recursion formula given in Ref. [4]:

$$F_m(t) = \frac{1}{2m+1} (2tF_{m+1}(t) + e^{-t}) \tag{6}$$

assuming that F_m vanishes for a high enough value of m , and the inverse relation, starting with a value of $F_0(t)$ with the necessary accuracy – by using the necessary terms in the expansion (6). The ranges of each method were chosen so as to optimize the corresponding computation time, for all five values of m , and with an error estimate of less than 10^{-8} , by comparison with the methods previously described.

The method employing recursion formula (6) was used for $t=0$ to a value of t ranging from 3 to 5, depending on its turn on the value of m . The number of times this formula had to be used increased very rapidly with t and was taken to be a simple stepfunction of t and m . The speed was considerably increased over that found using a fixed range of t and a minimum upper limit to this number of recursions. For $t = 3$ or 5 to $t = 16$, the inverse formula was used; the number of

terms in (5) was not sensitive to the values of t and m , and was finally taken to be 17 for this range. For t greater than 16, we could use Clenshaw's expansion for the complementary error function for the computation of $F_0(t)$; this converges very rapidly, and five terms were sufficient for the necessary accuracy for all values of m . However, we can also use the fact that $\text{erf}(\sqrt{t}) = 1$ to 11 digits for $t \geq 19.5$.

This integration program was used to check the integrals between Slater orbitals used during the previous calculation (Ref. [1]) and stored on magnetic tape. Using eight-term expansions, the differences were of the order to 0.00001 a.u. The computation of these integrals involving only Slater orbitals and their transformation to the corresponding ones for the orthonormal basis set was not necessary. This was because of the method used to orthogonalize the orbitals, and because these sets of transformed integrals had also been stored on magnetic tape during the previous calculation. This permitted the use of eight-term expansions for the Slater orbitals, for the rest of the necessary integrals. These also involved Gaussian functions, and no checks with tabulated values were available, but because of the method used, their accuracy was assumed to be at least as good as that of the other integrals.

A program was then written which assembled the small number of integrals required, and expanded this set into the smallest possible set which took no account of the symmetry of the system. The recurrence coefficients of the Schmidt process were then computed, and the recursion formulae derived from these used to transform the integrals into those corresponding to the orthonormal basis set. This procedure was preferred over the matrix transformation used in the previous calculation, as all the integrals did not have to be transformed. The matrix transformation method was nevertheless used for checking purposes, for a smaller basis set, and the two sets of transformed integrals proved to be identical to at least 4 digits. The coefficients of the wavefunction Ψ_0 were permanently stored, as well as the integrals from the previous calculation. The computation of the first row (and column) of the Hamiltonian matrix was carried out separately from the rest. This matrix was then diagonalized, and the nuclear repulsion terms added to the eigenvalues.

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