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Mixed Basis Functions in Molecular Quantum Mechanics

II. A Study of the H_2 Molecule

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A series of calculations for the ground state of the H_2 molecule are reported, using full configuration interaction method and a mixed orbital basis of 1*s* Slater and floating spherical Gaussian functions. The results obtained compare favourably with the results of previous H_2 calculations using pure Slater type orbital bases.

Es wird über eine Reihe von Rechnungen für den Grundzustand des H_2-Moleküls berichtet, bei denen eine Methode mit vollständiger Konfigurationswechselwirkung und eine gemischte Orbitalbasis aus 1*s* Slater- und "floating" spherischen Gauß-Orbitalen benutzt wird. Man erhält Resultate, die mit Ergebnissen von Rechnungen an H_2 mit Hilfe von Orbitalbasen reinen Slater-Typs vergleichbar sind.

Introduction

In the first paper of this series [1] the main ideas underlying the use of mixed basis sets were outlined as well as the basic computational methods. The results of some simple preliminary calculations on the He atom were also discussed.

In the present paper the results of a series of calculations on the H_2 molecule are summarized. This molecule is also treated in part as a test case. The basis sets consist of two 1*s*-type Slater orbitals on each nucleus and various combinations of spherical Gaussians positioned so as to be most effective as expansion functions. The calculations are of the full configuration interaction type within the framework of the Born-Oppenheimer approximation, for the ground state ($^1\Sigma_g$) of the H_2 molecule.

Calculations and Results

The details of the basis functions and the resulting energy terms are summarized in Tables 1 and 2, while in Figs. 1–4 the spatial arrangement of the Gaussian orbitals is shown. The first calculation, using a 1*s*, 1*s*′ STO-basis is identical to one reported by Shavitt *et al.* [2]. Since this basic set of four Slater functions was retained throughout all the other calculations the internuclear separation was kept constant at 1.4148 a.u. All the orbital exponents were optimized by Powell's method [3] in calculations Refs. [1] and [2], whereas in Refs. [3] and [4] the exponents of the STO's were kept constant at their previously determined optimum value. In calculations Refs. [6–9] only the exponents of

Table 1. The orbital bases used in the various H_2 calculations ($1S = 1s$-type Slater orbital, G = spherical Gaussian function)

Calculation Ref.	Number of basis functions	Number of configurations	Orbital basis, exponents and position of orbitals
1	4	6	$1S_A = 1S_B = 1.122$, $1S_{A'} = 1S_{B'} = 1.386$
2	5	9	$1S_A = 1S_B = 1.089$, $1S_{A'} = 1S_{B'} = 1.616$, $G_1 = 1.073$
3	6	12	$1S_A = 1S_B = 1.089$, $1S_{A'} = 1S_{B'} = 1.616$, $G_2 = G_3 = 1.115$, $d = 0.698$
4	6	13	$1S_A = 1S_B = 1.089$, $1S_{A'} = 1S_{B'} = 1.616$, $G_1 = 1.277$, $G_2 = 0.344$, $d = 0.7074$
5	7	16	$1S_A = 1S_B = 1.089$, $1S_{A'} = 1S_{B'} = 1.616$, $G_1 = 0.777$, $G_2 = G_3 = 0.655$, $d = 0.655$
6	9	16	$1S_A = 1S_B = 1.089$, $1S_{A'} = 1S_{B'} = 1.616$, $G_1 = 1.073$, $G_2 = G_3 = G_4 = G_5 = 0.570$
7	11	18	$1S_A = 1S_B = 1.089$, $1S_{A'} = 1S_{B'} = 1.616$, $G_1 = 1.073$, $G_2 = G_3 = G_4 = G_5 = G_6 = G_7 = 0.600$
8	13	13	$1S_A = 1S_B = 1.089$, $1S_{A'} = 1S_{B'} = 1.616$, $G_1 = 1.073$, $G_2 = G_3 = G_4 = G_5 = G_6 = G_7 = G_8 = G_9 = 0.600$
9	13	22	as for calculation Ref. [8]

Table 2. Summary of the H_2 calculations together with some "exact" results for comparison purposes

Calculation Ref.	Number of basis functions	Number of configurations	Total energy	Kinetic energy	Nuclear attraction energy	Electron repulsion energy	Energy of truncated NO expansion	Apparent correlation energy
1	4	6	−1.15279	1.15287	−3.61624	0.60376	−1.12805	−0.02474
2	5	9	−1.15898	1.15881	−3.62954	0.60493	−1.13209	−0.02689
3	6	12	−1.15923	1.16025	−3.63101	0.60472	−1.13208	−0.02715
4	6	13	−1.15953	1.16061	−3.63345	0.60649	−1.13241	−0.02712
5	7	16	−1.16003	1.15692	−3.62702	0.60325	−1.13260	−0.02743
6	9	16	−1.16865	1.16240	−3.62912	0.58966	−1.13223	−0.03642
7	11	18	−1.16883	1.16465	−3.62981	0.58952	−1.13222	−0.03661
8	13	13	−1.16882	1.16420	−3.62764	0.58781	−1.13210	−0.03672
9	13	22	−1.16992	1.16535	−3.62981	0.58773	−1.13215	−0.03777
"Exact" [5]			−1.174474					−0.040845
SCF calculation [6]			−1.133630				−1.133630	

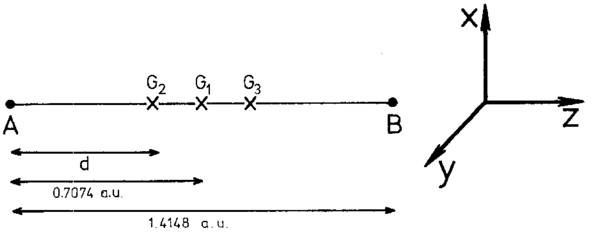

Fig. 1. Positions of the Gaussians in the 5, 6 and 7 orbital H_2 calculations [2–5]

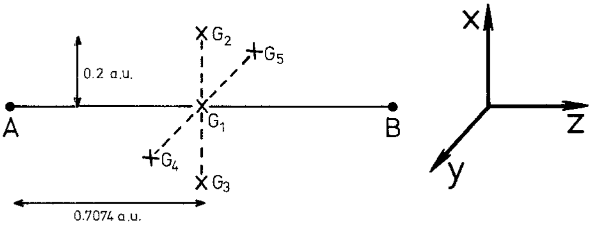

Fig. 2. Positions of the Gaussians in the 9 orbital H_2 calculation [6]

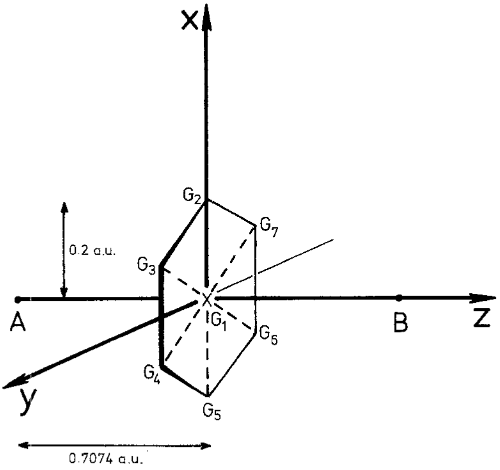

Fig. 3. Positions of the Gaussians in the 11 orbital H_2 calculation [7]

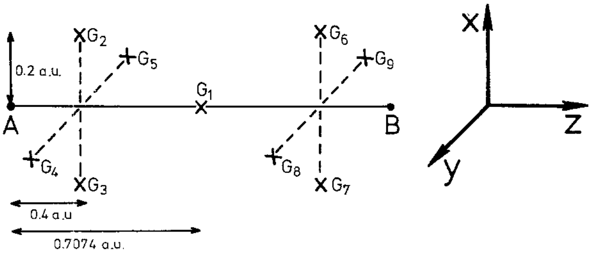

Fig. 4. Positions of the Gaussians in the 13 orbital H_2 calculations [8, 9]

Table 3. The wavefunction expressed in natural form from the 13 orbital, 22 configuration H_2 calculation, the representations of the D_{4h} point group, giving, in

Coefficient of configuration $\chi_i(1)\,\chi_i(2)$	Natural orbital χ_i and its symmetry	Coefficient of atomic orbital				
		S_{A}	$S_{\mathrm{A'}}$	S_{B}	$S_{\mathrm{B'}}$	G_1
0.990962	1 a_{1g} (σ_g)	0.440248	0.076852	0.440248	0.076852	0.0494282
−0.105193	2 a_{2u} (σ_u)	0.845793	0.115353	−0.845793	−0.115353	0.0
−0.056139	3 a_{1g} (σ_g)	−1.274842	0.852074	−1.274842	0.852074	0.662776
−0.041081	4 e_{1u_x} (π_{u_x})	0.0	0.0	0.0	0.0	0.0
−0.041081	5 e_{1u_y} (π_{u_y})	0.0	0.0	0.0	0.0	0.0
−0.009842	6 a_{2u} (σ_u)	−4.237023	3.268382	4.237023	−3.268382	0.0
−0.008768	7 e_{1g_x} (π_{g_x})	0.0	0.0	0.0	0.0	0.0
−0.008768	8 e_{1g_y} (π_{g_y})	0.0	0.0	0.0	0.0	0.0
−0.007305	9 a_{1g} (σ_g)	−1.722984	2.533367	−1.722984	2.533367	−2.816022
−0.006635	10 b_{1g} (Δ_g)	0.0	0.0	0.0	0.0	0.0
−0.006049	11 a_{1g} (σ_g)	−0.226189	−1.814420	−0.226189	−1.814420	−1.786898
−0.003339	12 b_{1u} (Δ_u)	0.0	0.0	0.0	0.0	0.0
−0.002578	13 a_{2u} (σ_u)	−1.844571	−2.184451	1.844571	2.189451	0.0

the off-axial Gaussians were optimized, while their distance from the molecular axis was kept constant at 0.2 a.u., this value having been found reasonable in our He calculations [1]. In calculation Ref. [8] the positions of the two sets of 4 Gaussians along the molecular axis were also determined so as to minimize the total energy. Full optimization of all non-linear parameters was not undertaken because of the limited computer time available for this work.

All the calculations were of the full configuration interaction type, the configurations constructed from a Löwdin orthonormalized set of symmetry orbitals, the point group of the molecule taken as $D_{\infty h}$ in all the calculations which use only σ-type orbitals. In calculations Refs. [6, 8, 9], i.e. when off-axial Gaussians were used as well, the point group of the molecule was taken to be D_{4h}, although the Gaussian lobe functions have close resemblance to the π- and Δ-type symmetry orbitals. Calculation Ref. [7] is more novel, since 6 Gaussians were placed around the molecular axis, forming a regular hexagon. The symmetry orbitals formed transform according to the irreducible representations of the D_{6h} point group. Calculations Refs. [8] and [9] differ inasmuch as the former makes use of only the π-type Gaussian lobe functions, whereas in calculation Ref. [9] the σ_g-, σ_u-, Δ_g- and Δ_u-type functions are included in the symmetry orbital basis. The wavefunctions were transformed to natural form, followed by the calculation of the energy corresponding to the dominant term in the expansion, furnishing an estimate of the SCF-energy as well as the apparent correlation energy, a concept introduced earlier [1].

The wavefunction, expressed in terms of natural orbitals, corresponding to the best H_2 energy, i.e. resulting from calculation Ref. [9], is presented in Table 3. The natural orbital expansion takes the form

$$\Psi = 2^{-1/2}(\alpha\beta - \beta\alpha) \sum_{i=1}^{13} C_i \chi_i(1)\,\chi_i(2)\,, \tag{1}$$

natural orbitals given in terms of the original basis. The orbitals are classified according to the irreducible brackets, the symmetry types they are to represent

Coefficient of atomic orbital							
G_2	G_3	G_4	G_5	G_6	G_7	G_8	G_9
0.002508	0.002508	0.002508	0.002508	0.002508	0.002508	0.002508	0.002508
0.142161	0.142161	0.142161	0.142161	−0.142161	−0.142161	−0.142161	−0.142161
0.053444	0.053444	0.053444	0.053444	0.053444	0.053444	0.053444	0.053444
1.678757	−1.678757	0.0	0.0	1.678757	−1.678757	0.0	0.0
0.0	0.0	1.678757	−1.678757	0.0	0.0	1.678757	−1.678757
0.026515	0.026515	0.026515	0.026515	−0.026515	−0.026515	−0.026515	−0.026515
7.054087	−7.054087	0.0	0.0	−7.054087	7.054087	0.0	0.0
0.0	0.0	7.054087	−7.054087	0.0	0.0	−7.054087	7.054087
0.161080	0.161080	0.161080	0.161080	0.161080	0.161080	0.161080	0.161080
10.83659	10.83659	−10.83659	−10.83659	10.83659	10.83659	−10.83659	−10.83659
0.683154	0.683154	0.683154	0.683154	0.683154	0.683154	0.683154	0.683154
45.5350	45.5350	−45.5350	−45.5350	−45.5350	−45.5350	45.5350	45.5350
1.960308	1.960308	1.960308	1.960308	−1.960308	−1.960308	−1.960308	−1.960308

where $\{\chi_i\}$ is the set of natural orbitals and $\{C_i\}$ is the set of coefficients, related to the occupation numbers of the NO's [1].

The wavefunctions from the other calculations are given elsewhere[1] [4].

Discussion

The addition of a single Gaussian to the four orbital basis results in a considerable lowering of the total energy, almost 4 kcal/mole, mostly as a result of the decrease in the nuclear attraction energy. Evidently the Gaussian has very successfully corrected the electron distribution in the molecule, which also shows up as an improvement in the energy of the dominant term of the natural orbital expansion. The decrease in the apparent correlation energy is less, indicating less improvement in the correlation part of the wavefunction than in the SCF part. The total energy −1.15898 a.u. compares favourably with the value −1.1591 a.u., calculated by Gianinetti *et al.*, who used a 1*s*, 2*s*, 2*p* STO-basis, 6 functions altogether [7]. Our six orbital calculations Refs. [3] and [4] are energetically superior to Gianinetti's calculation, although only marginally so. The result of the 7 orbital calculation [5], i.e. an energy of −1.16003 a.u., is to be compared with the estimated Σ limit of −1.160868 a.u. [8]. The discrepancy, ~1/2 kcal/mole, is small, considering the limited basis that was employed in this calculation. The SCF energy, as estimated by the energy of the truncated NO expansion, −1.13260 a.u., is in error by ~2/3 kcal/mole. The apparent correlation energy is, however, lower than the accurately calculated Σ correlation energy. As stated before [1], the apparent correlation energy, as defined, is not an upper bound to the true correlation energy, hence it needs to

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[1] The individual wavefunctions, expressed in terms of natural orbitals, are available from G. B. Bacskay, on request.

be used with some caution. It is interesting that all three Gaussians need to be in the internuclear region in order to minimize the total energy, indicating that the electron distribution needs most modification in that region and also that electron correlation is more important there. Originally two Gaussians were placed outside the internuclear region in an attempt to simulate the behaviour of two $2p_z$-type orbitals. This arrangement, however, proved inferior to the one described above. It would be interesting to investigate whether a $1s$, $2s$, $2p$ STO basis could be more successful if the p orbitals were allowed to float.

The introduction of π- and Δ-type Gaussian lobe functions bring about considerable improvement in the energy, mainly as a result of more electron correlation being allowed for. This is also manifested in the lowered electron repulsion energy. Our best energy, -1.16992 a.u., from calculation Ref. [9], is to be compared with the value -1.16959 a.u., calculated by Shavitt *et al.* [2], using a full $1s$, $1s'$, $2p$ STO-basis. The results of calculation Ref. [7], using 11 functions, with six Gaussians hexagonally around the molecular axis, are only as good as the results of the 13 orbital, 13 configuration calculation [8]. Consequently this approach of placing many Gaussians close together was not explored any further. Signs of approximate linear dependency also appeared in this calculation although no round-off errors are thought to be present in the results reported here. A comparison of the results from calculations Refs. [8] and [9] reveals that, although the π_u orbitals are the most important among the Gaussian lobe functions, the others also make a significant contribution to the wavefunction. The occupation numbers of the Δ_g and the extra σ_g orbitals, as inferred from the coefficients in Table 3, are fairly high, as expected.

Conclusion

The results of the various H_2 calculations have demonstrated that mixed basis sets containing both Slater and Gaussian type functions can provide just as satisfactory convergence as the more conventional STO bases.

The advantage of a mixed basis set is, however, the relative ease with which the basic integrals are evaluated. An increase in the size of the basis presents no problems other than the computer storage and manipulation of the large arrays that arise in the course of the calculations. With STO bases the introduction of atomic orbitals, higher than $2p$, involves so much extra effort as to prevent their extensive use in molecular calculations. The largest single H_2 calculation reported here, i.e. the 13 orbital, 22 configuration one, required approximately 7 min comp. time, and a total store of 40K on the Cambridge University Computer Laboratory's Titan computer – this comp. time being equivalent to less than 1 min on the more modern third generation computers.

A further advantage of the Gaussians as correction functions is that they can be allowed to float, i.e. be spatially positioned so as to be most effective, without any added computational problems. Hence strong localization of these correction functions is easily achieved.

In order to improve the 13 orbital wavefunction for H_2 two or more Gaussians placed along the molecular axis should be added to the basis, so as to obtain a better Σ limit than that of the 5 orbital calculation [2]. To improve the angular correlation more π- and Δ-type Gaussian lobe functions are needed. It is probable that φ-type functions would be much less important, as Davidson and Jones [9] obtained an energy of -1.173044 a.u. with the use of 10 natural orbitals, none of them higher than Δ.

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References

1. Bacskay, G. B., Linnett, J. W.: Theoret. chim. Acta (Berl.) **26**, 1—13 (1972).
2. Shavitt, I., Stevens, R. M., Minn, F. L., Karplus, M.: J. chem. Physics. **48**, 2700 (1968).
3. Powell, M. J. D.: The computer Journal **7**, 155 (1964).
4. Bacskay, G. B.: Mixed basis functions in molecular quantum mechanics. Ph. D. Thesis, Cambridge 1971.
5. Kolos, W., Wolniewicz, L.: J. chem. Physics **49**, 404 (1968).
6. — Roothaan, C. C. J.: Rev. mod. Physics **32**, 205 (1960).
7. Gianinetti, A., Majorino, G. F., Rusconi, E., Simonetta, M.: Int. J. quant. Chemistry **3**, 45 (1969).
8. Hagstrum, S., Shull, H.: Rev. mod. Physics **35**, 624 (1963).
9. Davidson, E. R., Jones, L. L.: J. chem. Physics **37**, 2966 (1962).

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