COLOPHON

The attached paper has no connection with my current research in Computer Science and Digital Documents. It is another in my series of experiments to see how long it takes me to re-build electronic versions of my published early papers as properly re-typeset 'PDF Normal' rather than just as a bitmap scan.

This particular paper appeared in the journal "Chemical Physics Letters" (Elsevier) in 1971. It is available online (to subscribers) as a scanned bitmap PDF via: `http://www.sciencedirect.com/`

The text was acquired by scanning the paper from an original pre-print and then using Omnipage OCR on the resulting TIFF files. The paper was then re-typeset using UNIX *troff* suite to set up the correct typeface (Times) and to get the line and page breaks as accurate as possible.

The diagram was extracted from the second TIFF page and after clean-up in Adobe Photoshop, it was then vectorized using Adobe Streamline. It was then imported into Adobe Illustrator 10.0, de-skewed, and exported in the format of version 3.2 of Illustrator's Encapsulated PostScript (but with no TIFF preview). This Encapsulated PostScript was then incorporated into the paper using *psfig* .

The time taken to rebuild this paper was about 3 hours.

3-BODY ENERGY TERMS IN A QUARTET STATE OF H_3

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Calculations of the 3-body energy term in a quartet ($^4A_2$) state of H_3 (equilateral triangle nuclear-configurations) show a minimum in the 3-body energy for a side length of about 1.3 bohrs.

There has been considerable interest in short range exchange interaction forces between atoms and in small molecules [1, 2]. While the theory of long range interatomic and intermolecular forces appears to be increasingly understood, many questions remain to be answered about the short range forces and more specifically about 2- and 3-body forces in such repulsive states [3] . We felt that a simultaneous study of the triplet $^3\Sigma_u^+$ state of H_2 and the quartet state of H_3 with the three lowest orbitals singly occupied (for a C_{3v}, configuration this is a $^4A_2$ state) might offer some light on the subject. In this note we include early results for the equilateral triangle configurations of H_3. A more detailed study will be published later.

Since the state of H_3 under consideration is a standard excited state [4] with 3 singly-occupied orbitals

$$E = \sum_i H_i + \sum_{i,j} (J_{ij} - K_{ij}).$$

Hence, with the obvious small modification from the ground state wavefunction formulation, the energy of this quartet state, in a variety of geometrical configurations, was determined using the method of "optimised floating spherical gaussians" [5] (see table 1). In this method a small number of spherical gaussians, generally free to float to any point of the configuration space, and limited only by the constraints imposed by the minimum energy principle, are taken as a basis set $\{\phi\}$ for an HF SCF calculation.

$$\phi_i = (2/\pi\rho_i^2)^{1/2} \exp[-(\mathbf{r}-\mathbf{R}_i)^2/\rho_i^2].$$

Table 1
2- and 3-body energies (in hartrees) for $H_2\,(^3\Sigma_u^+)$ and $H_3\,(^4A_2)$

Bond length (bohrs)	Energy of H_2 ($^3\Sigma_u^+$)	2-body energy [a]	Energy of H_3 ($^4A_2$) [c]	3-body energy [b]
0.5	0.1045	1.1031	1.8293	0.0179
0.75	-0.4028	0.5958	0.3020	0.0125
1.0	-0.6112	0.3874	-0.3910	-0.0553
1.5	-0.8005	0.1981	-0.99010	-0.0865
2.0	-0.8901	0.1085	-1.2381	-0.0657
3.0	-0.9681	0.0305	-1.4250	-0.0186

a) 2-body energy = energy of H_2 − energy of 2 isolated H atoms,

b) 3-body energy = energy of H_3 − single centre energy contributions − 2-body energy contributions.

c) An interpolated curve of the 3-body energy terms for $H_3(^4A_2)$ is shown in fig. 1.

The non-linear parameters, the $\mathbf{R}_i$ and ρ_i, are optimised [6] by minimising the total electronic energy. For the results reported here the basis set consisted of 4 concentric spherical gaussians fixed on each atomic centre and one gaussian fixed in the centre of each H-H bond (because of the symmetry of the configurations studied, this involved no artificial restriction on the models). In each calculation the nuclear framework was first set up, the basis added to it and the ρ_i optimised. Using four gaussians with numerically optimised exponents the total energy of a single hydrogen atom was found to be −0.4993 hartrees. For the $^3\Sigma_u^+$ state of H_2 the results were found to give over 99% of the total energy predicted in a definitive cal-
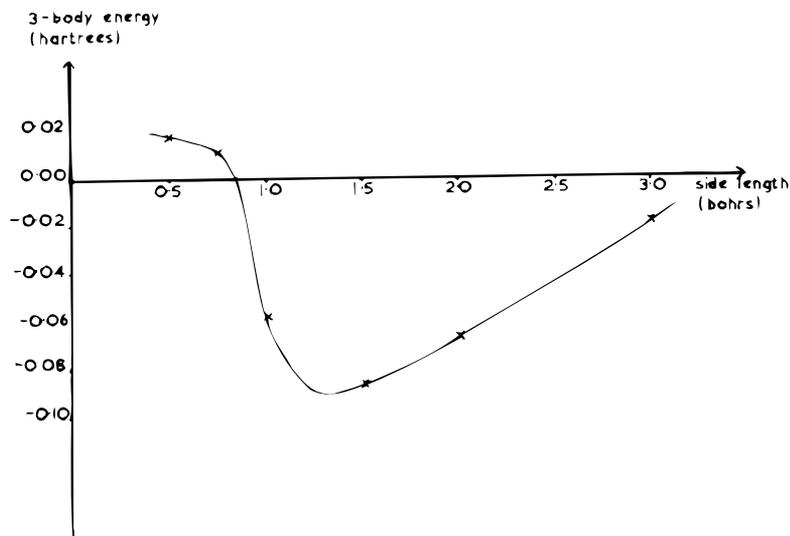
Fig. 1. Interpolated curve of the 3-body energy term for H_3 ($^4A_2$) in an equilateral triangle configuration.

culation which included all correlation effects etc. [3]. Further, since the $^4A_2$ state of H_3 is repulsive, we can reasonably expect the correlation to be smaller than in a general covalent state. We therefore expect the determined energies of the considered configurations of H_3 to be close to the Hartree-Fock limit.

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