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# Some valence bond calculations for $H_2$ with 1*s* and 2*p* basis sets

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**Summary.** The results of *ab initio* valence bond calculations are reported for $H_2$, with up to 16 nuclear centred and eight midbond 1*s* and 2*p* AOs included in them. The 24 AO calculation, with 116 $S = 0$ spin structures, gives an STO-6G energy of $-1.17237$ a.u., which is close to an MP4 estimate of $-1.17256$ a.u.

**Key words:** Valence bond – Hydrogen molecule

Although the results of MO-CI (molecular orbital-configuration interaction) calculations for the ground-state energy of $H_2$ abound, relatively few classical VB (valence bond) studies have been reported. In each of these VB calculations, nuclear-centred AOs (atomic orbitals) have been used [1–9], and the lowest VB energy that has been reported so far appears to be $-1.17001$ a.u. with 1*s*, 2*s* and 2*p* AOs [9]. The recent MO-CI studies by Wright and Barclay [10], which are equivalent to classical VB calculations with the same AO bases, have utilized midbond functions in some of their calculations. Here we report the results of various classical VB calculations that involve up to 24 1*s* and 2*p* AOs. Sixteen of these orbitals are nuclear centred ($1s_{a,b}$, $1s'_{a,b}$, $2p_{a,b}$ and $2p'_{a,b}$ with $1s_{a,b} = 1s_a$, $1s_b$ etc.) and the remainder are midbond functions ($1s_m$, $2p_m$, $1s'_m$ and $2p'_m$). All $S = 0$ spin structures have been included in the calculations, which were performed using the program prepared by Roso [11, 12]. A bond length of 1.4 a.u. was assumed.

The $1s_{a,b}$, $1s'_{a,b}$, $2p_{a,b}$, $1s_m$ and $2p_m$ exponents were energy optimized at the STO-5G level, and then held fixed in subsequent STO-5G and STO-6G calculations. Because the values of the optimized $1s_m$ and $2p_m$ exponents were found to be similar, the exponents for the $1s'_m$ and $2p'_m$ AOs were assumed to be equal. The $2p'_{a,b}$ AOs were optimized after the optimization of the $1s'_m$ and $2p'_m$ AOs. The resulting values for the exponents are as follows: $1s_{a,b} = 1.0_8$, $1s'_{a,b} = 1.5_3$, $1s_m = 1.4_9$, $2p_m = 1.5_5$, $2p_{a,b} = 1.9_6$, $1s'_m = 2p'_m = 2.6$ and $2p'_{a,b} = 1.5$.

In Table 1, we report the energies with different sets of AOs and different numbers of VB structures. The 14 AO calculation with four midbond functions generates an (STO-6G) energy of $-1.17114$ a.u., which is close to the MO-CI energy of $-1.171298$ a.u. reported by Wright and Barclay [10] with 21 nuclear-centred *s* and *p* functions. It is also substantially lower than the (non-optimized)

**Table 1.** VB energies (a.u) for $H_2$. The number of $S = 0$ spin structures is indicated in parentheses

| | STO-5G | STO-6G |
|---|---|---|
| $1s_{a,b}, 1s'_{a,b}$ (10) | $-1.15184$ | $-1.15226$ |
| $1s_{a,b}, 1s'_{a,b}, 2p_{a,b}$ (27) | $-1.16863$ | $-1.16904$ |
| $1s_{a,b}, 1s'_{a,b}, 2p_{a,b}, 2p'_{a,b}$ (56) | $-1.16972$ | $-1.17026$ |
| $1s_{a,b}, 1s'_{a,b}, 1s_m$ (15) | $-1.15714$ | $-1.15757$ |
| $1s_{a,b}, 1s'_{a,b}, 1s_m, 2p_m$ (22) | $-1.16693$ | $-1.16737$ |
| $1s_{a,b}, 1s'_{a,b}, 2p_{a,b}, 1s_m, 2p_m$ (47) | $-1.17072$[a] | $-1.17114$ |
| $1s_{a,b}, 1s'_{a,b}, 2p_{a,b}, 1s_m, 2p_m, 1s'_m, 2p'_m$ (73) | $-1.17156$[a] | $-1.17203$ |
| $1s_{a,b}, 1s'_{a,b}, 2p_{a,b}, 2p'_{a,b}, 1s_m, 2p_m, 1s'_m, 2p'_m$ (116) | $-1.17192$[a] | $-1.17237$ |

[a] The optimized exponents from these calculations were used in the remaining calculations. The exact energy is $-1.17447$ a.u. [14]

energy of $-1.17026$ a.u. for the 16 nuclear-centred AO calculation of Table 1. Inclusion of the eight midbond functions in the latter calculation lowers the energy to $-1.17237$ a.u., which is only slightly higher than the MP4 estimate of $-1.17256$ a.u. reported in [13], and lower than all MO-CI energies reported by Wright and Barclay with 26 or less $s$ and $p$ type AOs. Of course, better $p$-type AOs—for example $3p$ rather than $2p$ [7], and $p\sigma$ exponents that differ from those for the $p\pi$ and $p\pi'$ AOs [6]—would produce lower energies in each of the VB calculations that involve $p$-type AOs, but this aspect has not been examined here. It may be noted that exclusion of all ionic structures raises the 24 AO energy from $-1.17237$ a.u. to $-1.16915$ a.u.

Substantial improvements in energy are obtained by including additional types of AOs, i.e. $d, f$ and $g$ AOs, and by increasing the number of atomic centres on which the AOs may be located. We have performed some pilot studies of the latter option, with two "outer" (o) and two "inner" (i) $1s$ AOs, located as $1s^o_a H^+_a 1s^i_a 1s^i_b H^+_b 1s^o_b$, with the distances, $r(1s^o\text{-}H^+)$ and $r(H^+\text{-}1s^i)$, and the orbital exponents determined variationally. The optimized (STO-6G) energy occurs when $r(1s^o\text{-}H^+) = 0.02$ a.u., $r(H^+\text{-}1s^i) = 0.08$ a.u., $\zeta^o = 1.06$ and $\zeta^i = 1.35$. This energy, $-1.15639$ a.u., is substantially lower than the $-1.15249$ a.u. that is obtained when the four AOs are nuclear centred, with $\zeta = 1.11$ and $\zeta' = 1.40$. Because our program does not currently permit more than six atomic centres to be included in the calculations, it was not possible to perform a 24 AO calculation with sixteen inner and outer AOs and eight midbond AOs, but the results of the present four AO study suggest that the resulting energy could lie below $-1.173$ a.u. If this is the case, this energy would be comparable with MO-CI energy of $-1.17303$ a.u. calculated by Wright and Barclay with 34 nuclear-centred and midbond $s$ and $p$ type functions.

Finally, to investigate further the effect of increasing the number of atomic centres, a 27 AO calculation was performed, with three additional $1s$ AOs located in the midplane at the corners of an equilateral triangle, each corner at a distance of 0.6 a.u. from the bond centre. The exponents for these AOs were set equal to the 1.08 for two of the nuclear centred $1s$ AOs. The resulting energy is $-1.17268$ a.u.

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