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Full CI Calculations of Magnetic Properties of the H_2 Molecule in the $B^1\Sigma_u^+$ State*

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The magnetizability, the g-factor, the NMR shielding constant and the spin-rotation constant of the hydrogen molecule in the $B^1\Sigma_u^+$ state are studied in the full Configuration Interaction (full CI, FCI) approach. A GIAO orbital basis is used to ensure gauge-origin indepedence of the computed properties. Their dependence on basis set and internuclear distance is analysed. Our results for the magnetizability confirm that this excited state of H_2 is paramagnetic. The paramagnetism of this state is also reflected by the values of the other properties.

Key words: NMR, shielding constant, magnetizability, hydrogen molecule, GIAO orbitals, paramagnetism

1. INTRODUCTION

The full CI method has recently been succesfully used to compute magnetic properties of the hydrogen molecule in its ground state [1–3]. The calculated magnetizability ξ, g-factor g, hydrogen NMR shielding constant σ, and spin-rotation constant $\mathcal{M}$ are in agreement with the experimental data and with other *ab initio* results. The full CI results are among the most accurate values for all these properties. The magnetic properties of the ground state are thus well known.

In contrast, little is known about the magnetic properties of the excited states of H_2. In their *ab initio* calculations, Rychlewski and Raynes used explicitly correlated wavefunctions to compute the magnetizability and the g-factor for some of the excited states of H_2 [4–6]. In particular, they have shown that the H_2 molecule is paramagnetic in the lowest excited singlet state, $B^1\Sigma_u^+$. There are, to our knowledge, no experimental data to confirm this finding. Also, no information – experimental or theoretical – is available for the shielding or the spin-rotation constant. Considering the very good performance of the full CI approach for the ground state, we decided to study the magnetic properties of the $B^1\Sigma_u^+$ state in the same approximation.

2. COMPUTATIONAL ASPECTS

The FCI approach provides, as is well known, the exact solution to the problem of computing a wavefunction within a chosen orbital space. For the calculation of second-order molecular properties, we use the solution of the first-order response

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equations, which for a FCI wavefunction corresponds to a full sum-over-states calculation in the given configuration space. Thus, the accuracy of the results is determined by the choice of the basis set only.

In this work, we have used the augmented correlation-consistent basis sets of Refs. [7,8]. The calculated magnetic properties are gauge-origin independent as GIAOs (gauge-invariant atomic orbitals) [9,10] have been used in all the calculations.

At the FCI level, we used the aug-cc-pVTZ, daug-cc-pVTZ and taug-cc-pVTZ basis sets to test the convergence of the computed properties. The largest basis set which was finally chosen for our calculations, taug-cc-pVTZ, is a [8s5p4d/6s5p4d] basis consisting of 82 CGTO functions (spherical sets of d and f functions are used). The resulting CI expansion contains 539 configurations (of proper spin and space symmetry). At the SCF level, we have in addition used the augmented cc-pVQZ sets, the largest one being the daug-cc-pVQZ [8s5p4d3f/6s5p4d3f] set including 124 CGTOs (this set differs significantly from taug-cc-pVTZ, the QZ sets have different exponents from the TZ sets).

To illustrate our basis set analysis we use the results for the perpendicular component of the magnetizability, $\xi_\perp$, and for the g-factor at an internuclear distance of 2.5 a.u., close to the minimum of the potential. We present only the data for the largest basis sets to show that the results are practically converged. At the FCI level, the differences between the properties computed for the daug-cc-pVTZ and taug-cc--pVTZ basis sets are about 1%: we obtain for $\xi_\perp$ 4.6020 and 4.5534 a.u., and for the g-factor -10.2340 and -10.1475, respectively. The corresponding SCF results obtained using the daug-cc-pVTZ, taug-cc-pVTZ and daug-cc-pVQZ sets are for $\xi_\perp$ 5.0692, 5.0312 and 5.0911 a.u., and for g -11.65, -11.57 and -11.64, respectively. Not only are these SCF values in good agreement with each other, they also indicate that the correlation corrections are relatively small, about 10% for $\xi_\perp$ and about 15% for the g-factor. Thus, we do not think that further extensions of the basis set would change the SCF or the FCI values significantly.

As an additional test, we have used the taug-cc-pVTZ basis set to perform FCI calculations of all the properties for the ground state at R =1.4 a.u. Our results — ξ = -0.8329 a.u., g = 0.8803, σ = 26.708 ppm and $\mathcal{M}$ = 117.20 kHz — are in very good agreement with the literature data, the differences being smaller than 1.5% (see Refs. [1–3] for a discussion of the ground state values calculated in the FCI approach and the works of Rychlewski *et al.* [11,12] for results obtained with explicitly correlated wavefunctions).

Finally, we can compare the full CI energies with other available results. For the $B\,^1\Sigma_u^+$ state in the region of the minimum, our taug-cc-pVTZ energies agree with Kołos and Wolniewicz [13] with sufficient accuracy, being about 0.001 a.u. higher. The minimum is at 2.42 a.u., to be compared with the experimental value of 2.43 a.u. We have also checked, for a few selected internuclear distances, the energy of the lowest excited state which contributes to the magnetizability in a sum-over-states formulation — that is, the $C\,^1\Pi_u$ state. As for the reference state, our FCI energies are about 0.001 a.u. higher than the energies given by Kołos and Wolniewicz [14]. We believe that these differences in energy are so small that any further improvement of the calculated energies could not be directly related to an improvement of the accuracy of the calculated magnetic properties.

All the calculations have been performed using the DALTON program system [15].

3. RESULTS AND DISCUSSION

In Table 1, we present our results for the magnetizability tensor and for the g factor for a range of internuclear distances, comparing them with the results of Rychlewski and Raynes [5]. Following the procedure of Ref. [5], we have tabulated the values of g^e, the electronic contribution to the g factor (the nuclear contribution is constant and for H_2 $g^N = 0.9995$). The parallel component of the magnetizability (computed in both formulations as a purely diamagnetic term) agrees with the values obtained earlier [5] to within 2% for all the distances up to R= 5.0 a.u. For the perpendicular component and the g factor — which are determined by the first-order perturbed function — the differences are larger and we discuss them in more detail in the next section. Nevertheless, the general trends in the geometry dependence of these properties are similar in the two studies. We find that the sign of the total magnetizability changes with R and that this state is paramagnetic in the region of the minimum, in accordance with the results of Rychlewski and Raynes [5].

Table 1. Magnetizability and g^e factor.

R	$\xi_{\parallel}$ This work	$\xi_{\parallel}$ Ref. [5]	$\xi_{\perp}$ This work	$\xi_{\perp}$ Ref. [5]	ξ This work	ξ Ref. [5]	$-g^e$ This work	$-g^e$ Ref. [5]
1.8	−2.4536	−2.4441	11.9050	4.8767	7.1188	2.4364	41.4345	21.53548
2.0	−2.3153	−2.3505	8.9127	4.8323	5.1700	2.4380	27.0852	18.88371
2.2	−2.1928	−2.1812	6.7711	4.3777	3.7832	2.1914	18.4844	14.44891
2.4	−2.0910	−2.0750	5.1908	3.8405	2.7635	1.8687	13.0853	11.13388
2.5	−2.0485	−2.0315	4.5534	3.5080	2.3527	1.6620	11.1470	9.73960
2.7	−1.9801	−1.9588	3.5139	2.8717	1.6826	1.2615	8.2848	7.52207
3.0	−1.9150	−1.8893	2.4099	2.1461	0.9683	0.8010	5.6382	5.35977
4.0	−1.9321	−1.9044	0.7525	0.7274	−0.1423	−0.1499	2.4499	2.42183
5.0	−2.1474	−2.1116	0.0940	0.0265	−0.6531	−0.6862	1.6089	1.57791
7.0	−2.7622	−2.6850	−0.1833	−0.6557	−1.0429	−1.3321	0.6878	1.10338
10.0	−3.8447	−3.7386	6.8124	2.0809	3.2600	0.1411	1.5512	1.17035

[a] We use atomic units for the magnetizability, thus the results of ref. [5] are multiplied by 0.5. Also, more decimal figures are given in [5].

Our results for the hydrogen shielding constant and for the spin-rotation constant are shown in Table 2. These properties have been calculated using the same first-order perturbed wavefunction we used for the magnetizability and the g-factor. Not surprisingly, the dependence on R is similar to that observed for ξ and g.

Using the programs available in the MOLCAS package [16], we have estimated the rovibrational corrections to the computed properties. For rovibrational averaging we have used our own potential energy curve, which is sufficiently accurate as indicated by the calculated rovibrational constants. For example, we find $G_V = 687.58$ and 2005.04 cm^{-1} for the lowest two vibrational states, to be compared with 674.22

and 1992.62 cm^{-1} reported in Ref. [17]. The results of the averaging for the lowest rovibrational states are shown in Table 3. The differences between the interpolated equilibrium values obtained in the rovibrational averaging procedure (ξ = 2.6717 a.u., g = -11.6390, σ = -6.0185 ppm and $\mathcal{M}$ = 105.1444 kHz) and the v=0, J=0 values are rather small. The dependence of g and $\mathcal{M}$ on the internuclear distance is significantly different for small and large R values, leading to larger averages of these properties for v=1 than for v=0.

Table 2. NMR shielding constant and spin-rotation constant.[a]

R	σ This work	$\mathcal{M}$ This work
1.8	–24.7549	–370.2695
2.0	–16.7759	–237.4435
2.2	–10.8798	–158.3744
2.4	–6.4238	–109.1906
2.5	–4.6053	–91.6743
2.7	–1.6027	–65.9249
3.0	1.6893	–42.0885
4.0	6.8866	–13.1227
5.0	8.3139	–6.1016
7.0	7.7788	–3.0290
10.0	–4.2047	–5.1874

[a] σ in ppm, $\mathcal{M}$ in kHz.

Table 3. Rovibrational averages.[a]

v,J	ξ	g	σ	$\mathcal{M}$
0,0	2.560	–11.73	–5.45	–106.2
0,1	2.543	–11.64	–5.37	–105.5
1,0	2.405	–12.02	–4.61	–109.3
1,1	2.388	–11.94	–4.54	–108.4

[a] ξ in a.u., σ in ppm, $\mathcal{M}$ in kHz.

4. ANALYSIS OF THE RESULTS

Since the difference between our results and those of Rychlewski and Raynes is larger than we expected, we have performed some additional calculations. For comparison with their work [5], we have performed FCI calculations at R=2.5 a.u. using standard field-independent atomic orbitals. We obtained results very similar to those with GIAO orbitals. We can compare directly the results of this calculation for $\xi_\perp^d$ = -4.1599 and $\xi_\perp^p$ = 8.7494 a.u. with the corresponding values of Ref. [5], -4.1011 and 7.6091 a.u. The difference is, as one could expect, in the paramagnetic part $\xi_\perp^p$, and amounts to about 15% of the total value. However, since there is a significant cancellation of the diamagnetic and paramagnetic terms, the difference becomes much more noticeable in the total value of ξ, $\xi = \xi^d + \xi^p$.

As mentioned above, our $B^1\Sigma_u^+ \rightarrow C^1\Pi_u$ excitation energy for internuclear distances close to the minimum agrees with that obtained using explicitly correlated wavefunctions, the excitation energy being about 0.05 a.u. and the differences less than 0.001 a.u.. These differences are too small to explain the discrepancy between our results for magnetic properties and those obtained with explicitly correlated wavefunctions by Rychlewski and Raynes. For example, even though our FCI energy for the ground state is 0.0018 a.u. (399 cm^{-1}) above the best results, the computed properties are in good agreement with the explicitly correlated wavefunction values. We find it unlikely that any changes in our basis set would significantly modify the SCF values or increase the computed correlation effects by a factor of 2 or 3, – as would be needed to bring our results into agreement with Rychlewski and Raynes.

The explicitly correlated wavefunctions have been most successful in the determination of accurate lowest electronic states for each of the considered symmetries of H_2 molecule. However, the magnetic properties are given (in the sum-over-states formulation, appropriate for both the FCI scheme and the explicitly correlated approach) by a perturbation expression including an infinite summation over all the excited states. The accuracy of the calculated properties depends more strongly on the flexibility (number of terms) in the expansion which are used than on the description of the lowest-lying electronic states. Specifically, in our case it may be more important that for the perturbation expansion our $^1\Pi_u$ space consists of 414 configurations, whereas in the expansion of paper [5] there are only 64 terms. In our opinion, this may be insufficient to provide the flexibility needed to describe the first-order perturbed wavefunction – noting that magnetic perturbations are notoriously difficult to describe.

In summary, we confirm the paramagnetism of the $B^1\Sigma_u^+$ state. We believe that our results for the magnetizability and for the g factor may be more accurate than those previously reported. We have also presented the first results for the shielding and spin-rotation constant. They differ from the corresponding ground state values in sign, and this is related to the paramagnetism of the $B^1\Sigma_u^+$ state. The spin-rotation constant is a property experimentally accessible, it is determined in molecular beam experiments. It may therefore be possible to indirectly verify the paramagnetic character of the $B^1\Sigma_u^+$ state experimentally by measurements of the spin-rotation constant of the molecule in this excited state.

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