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Magnetic properties of the BH molecule*

A CASSCF study

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Summary. The magnetic susceptibiliy of the BH molecule, as well as the magnetic shielding at the boron nucleus, have been calculated using CASSCF wavefunctions. A variety of active spaces have been employed, thus including more and more dynamical correlation. With very large active spaces, nearly all the valence correlation can be retrieved. The effect of core correlation is discussed in a second series of calculations and found to be small. Final results are $+12.5$ ppm cgs for the susceptibility and -175 ppm for the magnetic shielding at the boron nucleus.

Key words: BH – CASSCF – Magnetic shielding

1 Introduction

Although not known from experiment, the magnetic properties of the BH molecule, especially its magnetic susceptibility, have constantly been a topic of research during the last 25 years. The great interest in BH stems from the fact that this molecule is (van Vleck-) paramagnetic despite its (closed-shell) singlet ground state.

This has been found for the first time by Stevens and Lipscomb [1] at the coupled Hartree-Fock (CHF) level. At that time, this was a surprise, since there had been a firm belief that a closed-shell singlet molecule should be diamagnetic. 'Proofs' for this [2, 3] are only valid for one- and two-electron systems [4, 5] and therefore not applicable to the BH molecule. An explanation why BH is paramagnetic at the Hartree-Fock level is also given in [6].

Subsequently, there have been other CHF calculations on BH [7–10]. Provided a sensible gauge origin (at the boron nucleus or at the center of mass) is chosen, it is no problem to choose basis sets that give results close to the Hartree-Fock limit at least for the magnetic susceptibility χ and the magnetic shielding at the boron nucleus, σ(B). The Hartree-Fock limit is about $+18.5$ ppm cgs for χ and -260 ppm for σ(B).

There have been some correlated calculations of the magnetic susceptibility of BH. In 1978, Jaszunski [11] employed MCSCF wavefunctions in the active spaces

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$4\sigma 2\pi$ and $6\sigma 2\pi$. Due to some restrictions in the wavefunctions, he had to impose additional approximations on the perturbation scheme which lead to two different variants. His results span the range from 10.7 to 14.4 ppm cgs.

The next attempt was made by Corcoran and Hirschfelder [12] in 1980. They used CI wavefunctions and a *sum over states* formula. For the magnetic susceptibility, they obtained 6.0 ppm, so χ is considerably reduced. One can argue that their result is too small since a *sum over states* expansion converges slowly and extending the CI space can only increase the susceptibility.

In 1983, Daborn and Handy [13] calculated the magnetic susceptibility of BH with a coupled MC-SCF (CMSCSF) scheme using a CASSCF wavefunction in the active space $4\sigma 1\pi$. Again, the magnetic susceptibility (+9.81 ppm) is found to be much smaller than at the Hartree-Fock level. At the same time, Iwai and Saika [14] tried to investigate the correlation effects on the magnetic properties of BH with an MBPT analysis. Unfortunately, they essentially got the difference between uncoupled and coupled Hartree-Fock (see also [15]).

Recently, Sauer, Oddershede and Geertsen [16] reviewed the magnetic susceptibility of BH. They presented extensive basis tests and calculated χ at the Hartree-Fock level (18.5 ppm) and using the SOPPA (20.6 ppm) and CCPPA (15.5 ppm) (polarization propagator) formalisms. In all cases, their 'origin-independent' approach [17] has been used, but this should make no difference since their biggest basis is close to saturation. While the SOPPA calculations fail completely and even predict the wrong sign of the correlation correction, the CCPPA values are more in agreement with the other results.

To my knowledge, correlated calculations of the magnetic shielding at the boron nucleus have only been reported within a review of the SOPPA method [18]. The value reported for a SOPPA calculation is −298.2 ppm. Again, SOPPA even fails to predict the sign of the correlation correction. The corresponding CCPPA value is given as −215.3 ppm.

A calculation of de la Vega et al. [19] using a method developed by Hameka [20] reports BH to be diamagnetic. This calculation is certainly in error.

For the convenience of the reader, a compilation of selected literature values, along with the results obtained in the present study, can be found in Table 3. The interatomic distance varies from 2.329 a_0 to 2.336 a_0 in these calculations.

Since an adequate treatment of electron correlation is so crucial in this molecule, I will report the results of CASSCF calculations with a single (but reasonable) basis set, employing a variety of active spaces. The hydrogen shieldings have not been studied since their dependence on electron correlation is much less pronounced.

2 Basis set, computational aspects

Extensive basis tests, including those of [16], have been performed at the SCF and CASSCF (full valence CAS) level. A basis set which gave reasonable results in both cases has been chosen for further investigations:

At the boron atom, this is an $11s7p$ Huzinaga basis contracted to (41111111, 211111), augmented by four sets of d-functions with exponents 0.125, 0.5, 2.0 and 8.0 and two sets of f-functions with exponents 0.5 and 1.0. A $10s$ Huzinaga basis, contracted to (31111111), has been chosen for the hydrogen atom. It has been augmented by four p-sets (0.1, 0.3, 0.9, 2.7) and two d-sets (0.2, 0.8). The primitive functions are real spherical harmonics, and the total number of basis functions is 90.

The SCF energy (at the distance 2.336 a_0) obtained with this basis set is $-25.1312\ E_h$, which is close to the numerical Hartree-Fock value, $-25.1316\ E_h$ [21]. When shifting the gauge origin from the boron to the hydrogen nucleus, the computed values for χ and σ(B) change from 18.51 to 18.49 ppm cgs and -262.9 to -263.5 ppm at the CHF level. At the CMCSCF level with a full valence CAS, χ changes from 9.85 to 9.70 ppm cgs at the same time, while σ(B) happens to be the same (139.3 ppm) for either choice of the gauge origin. MC-IGLO values [27] are very close to these results, especially to those obtained with a common gauge origin at the boron nucleus.

Evaluating magnetic properties by the CMCSCF method is equivalent to the calculation of the linear response of an MCSCF wavefunction to a static magnetic field [22, 23]. In the case of CASSCF wavefunctions, the theory has been developed by Daborn and Handy [13]. This method has been implemented on top of an MCSCF program by Werner and Knowles [24, 25] which is part of the MOLPRO system [26]. All calculations have been performed with a gauge origin at the boron nucleus. This is a special application of the MC-IGLO program (which normally uses distributed gauge origins) described elsewhere [27]. The program can handle CI expansions with $\sim 10^6$ Slater determinants on current computers.

Throughout this paper, the magnetic susceptibility is given in units of ppm cgs[1]. Positive values ($\chi > 0$) mean paramagnetism. Magnetic shieldings are dimensionless values and are given in units of 10^{-6} (ppm). This value corresponds to an NMR chemical shift with respect to the 'naked' nucleus. Positive values indicate shielding, negative values deshielding.

3 Results and discussion

In Table 1, the energy and magnetic properties of BH are given for some selected active spaces. The 1σ orbital has been kept inactive (doubly occupied in all Slater determinants) in this first series of calculations. Since only four correlating electrons remain, it is possible to go to very large active spaces and hence to include

Table 1. Results for selected active spaces. 1σ orbital kept inactive. For units and sign convention see end of Sect. 2

occ. orbit.	Energy	$\chi_\perp$	$\chi_\parallel$	χ	$\sigma_\perp$(B)	$\sigma_\parallel$(B)	σ(B)
3σ	-25.13120	33.72	-11.92	18.51	-493.71	198.81	-262.87
$4\sigma 1\pi$	-25.18712	20.62	-11.69	9.85	-308.62	199.70	-139.18
$4\sigma 2\pi$	-25.20399	21.06	-11.71	10.14	-309.82	199.75	-139.96
$6\sigma 2\pi$	-25.21917	21.41	-11.88	10.31	-317.17	199.65	-144.90
$7\sigma 2\pi$	-25.22228	23.17	-11.83	11.50	-342.21	199.63	-161.60
$8\sigma 3\pi$	-25.22730	22.86	-11.81	11.30	-335.89	199.68	-157.37
$9\sigma 3\pi 1\delta$	-25.22858	24.48	-11.82	12.38	-358.02	199.70	-172.11
$9\sigma 4\pi 1\delta$	-25.22930	24.37	-11.83	12.30	-357.19	199.71	-171.56
$10\sigma 4\pi 1\delta$	-25.22970	24.46	-11.84	12.36	-359.42	199.71	-173.04
$10\sigma 5\pi 2\delta$	-25.23125	24.65	-11.83	12.49	-361.93	199.71	-174.72
$12\sigma 6\pi 3\delta$	-25.23287	24.68	-11.83	12.51	-362.10	199.71	-174.83

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[1] 1 ppm cgs $= 4.7519\ e^2 a_0^2 m_e^{-1} = 3.7497 * 10^{-28}\ JT^{-2}$

more and more dynamical correlation. This idea has also been pursued by Roos in a different context [28].

The active spaces were chosen such that the smallest occupation number in each symmetry has the same order of magnitude. This decision has been taken to avoid an unbalanced treatment of electron correlation. The 3σ occupied space just leads to the SCF wavefunction, while the $4\sigma 1\pi$ occupied space is a full valence CAS.

The largest occupied space yields a correlation energy of $-0.102\ E_h$ and picks up nearly all the valence correlation: a four-electron *full CI* calculation (with MCSCF orbitals) in a slightly smaller basis ($E_{\mathrm{SCF}} = -25.1311\ E_h$) gives a correlation energy of $-0.103\ E_h$. Both values are in good agreement with the value ($-0.100\ E_h$) calculated by Meyer and Rosmus [29].

It is not surprising that the tensor components of χ and σ(B) parallel to the molecular axis only show a small correlation effect and are already well calculated at the SCF level. These numbers are simply expectation values of the ground state wavefunction since the linear response term (the 'paramagnetic' term) vanishes by symmetry.

While it is not unexpected that the SCF wavefunction gives the most paramagnetic results, it is noteworthy that the most diamagnetic results are obtained with the full valence CAS. Obviously, the correlation effect is overestimated at that level, something that has also been observed in other cases [23, 27, 30].

When enlarging the active space, a convergence towards a magnetic susceptibility of $+12.5$ ppm cgs and a σ(B) of -175 ppm can be observed. It can be seen that adding a δ-function to the active space has a notable effect on the calculated magnetic properties. Since one could argue that the basis set is too small to account for this effect, the calculations on the active spaces $8\sigma 3\pi$, $9\sigma 3\pi 1\delta$ and $9\sigma 4\pi 1\delta$ have been repeated with a better polarized basis set ($11s7p6d3f/10s6p3d$). The results are practically the same as in Table 1.

So far, the 1σ orbital has been kept inactive in the calculations. The 'exact' correlation energy estimated by Meyer and Rosmus [29] amounts to $-0.152\ E_h$, and $-0.148\ E_h$ is retrieved in their calculation. These figures demonstrate that the core contributes considerably to the total correlation energy. Jaszunski [11] argues that the effect of core correlation on the magnetic susceptibility is small since the 1σ orbital contributes very little to χ. If this is a valid argument, it can also be applied to σ(B): the diamagnetic contribution from the 1σ orbital is not very sensitive to electron correlation and its paramagnetic contribution to σ(B) is small (~ 0.1 ppm). However, such an argument must be used with care.

In Table 2, there are the results of another series of calculations, but all six electrons are correlated this time. Because we are interested in core correlation now, the occupation number of the 1σ orbital has been tabulated as well. Its deviation from the closed-shell value (2.0) indicates how much the 1σ orbital is correlated. Unfortunately, the higher number of electrons makes these calculations much more demanding, so I was not able to use as large active spaces as in Table 1.

When using small active spaces (up to $6\sigma 2\pi$), it does not make much difference whether one keeps the 1σ orbital inactive or not since no orbitals which correlate the core enter the active space. The occupation number of the core orbital is very close to 2.0, and the energy as well as the magnetic properties do not differ much from those obtained with the 1σ orbital kept inactive.

Going from $6\sigma 2\pi$ to $7\sigma 2\pi$, one σ-orbital with a high orbital energy ($+14.2\ E_h$) enters the active space. This has not been observed in all the calculations with an inactive core. The 1σ occupation number drops considerably, and the energy is lowered by as much as $0.015\ E_h$. This certainly means that a σ-orbital which

Table 2. Results for selected active spaces. All electrons are correlated. For units and sign convention see end of Sect. 2

occ. orbit.	Energy	$n\,(1\sigma)$	$\chi_\perp$	$\chi_\parallel$	χ	$\sigma_\perp(\mathrm{B})$	$\sigma_\parallel(\mathrm{B})$	$\sigma(\mathrm{B})$
3σ	−25.13120	2.0000	33.72	−11.92	18.51	−493.71	198.81	−262.87
$4\sigma 1\pi$	−25.18720	2.0000	20.63	−11.69	9.85	−308.81	199.70	−139.31
$4\sigma 2\pi$	−25.20410	2.0000	21.09	−11.71	10.16	−310.19	199.75	−140.21
$6\sigma 2\pi$	−25.21969	1.9999	21.44	−11.87	10.34	−318.92	199.65	−146.07
$7\sigma 2\pi$	−25.23343	1.9992	21.46	−11.88	10.35	−319.26	199.64	−146.30
$8\sigma 2\pi$	−25.23672	1.9992	22.91	−11.83	11.33	−340.81	199.62	−160.67
$8\sigma 3\pi$	−25.24030	1.9992	23.43	−11.81	11.68	−344.89	199.65	−163.38
$9\sigma 3\pi$	−25.24781	1.9987	22.96	−11.81	11.37	−338.63	199.61	−159.22
$9\sigma 3\pi 1\delta$	−25.24863	1.9987	24.23	−11.81	12.22	−356.40	199.64	−171.06
$9\sigma 4\pi$	−25.26215	1.9978	23.02	−11.80	11.41	−340.92	199.61	−160.74
$9\sigma 4\pi 1\delta$	−25.26299	1.9978	24.52	−11.80	12.41	−361.82	199.64	−174.67

Table 3. Selected literature values for the magnetic properties of BH. For units and sign convention see end of Sect. 2

a) Hartree-Fock calculations	χ	$\sigma(\mathrm{B})$	E_{SCF}
Hegstrom and Lipscomb [7]	18.8	−262	−25.1291
Fowler and Steiner [10]	18.5	−258	−25.12986
Sauer et al. [16]	18.5		−25.13141
This work	18.5	−263	−25.13120

b) correlated calculations	χ	$\sigma(\mathrm{B})$	Method
Jaszunski [11] (Method A)	10.7		MCSCF
Jaszunski [11] (Method B)	13.4		MCSCF
Corcoran and Hirschfelder [12]	6.0		CI
Daborn and Handy [13]	9.8		CASSCF
Sauer et al. [16]	15.5		CCPPA
Oddershede and Sabin [18]		−215	CCPPA
This work	12.5	−175	CASSCF

primarily correlates the core has entered the active space. It is important to note that the magnetic properties remain almost the same, so this is a first hint that core correlation may not be important for these properties.

Going from $7\sigma 2\pi$ to $8\sigma 2\pi$ corresponds to going from $6\sigma 2\pi$ to $7\sigma 2\pi$ in Table 1, except for the additional core-correlating orbital that is present here. The energy changes very little and the magnetic properties change considerably, but exactly in the same way they did in the first series of calculations. Again, the inclusion of core correlation lowers the energy substantially but does not change the magnetic properties.

The largest active spaces in Table 2 contain more core-correlating orbitals: there are two of σ-symmetry in the $9\sigma 3\pi$ and $9\sigma 3\pi 1\delta$ active spaces and even two of σ-symmetry and one pair of π-symmetry in the $9\sigma 4\pi$ and $9\sigma 4\pi 1\delta$ active spaces.

The effect of adding a δ-function is just the same as in Table 1, and again, this does not change when using a bigger basis set. Going from $9\sigma 3\pi 1\delta$ to $9\sigma 4\pi 1\delta$ adds a core-correlating pair of π-orbitals to the active space, which has a major influence on the energy. But the magnetic properties only differ little. It is perhaps not justified to extrapolate Table 2 to the full CI limit, but it is obvious that core correlation does not have a sizeable influence on the magnetic properties studied here.

4 Conclusions

Extending the active space in a CASSCF calculation is, at least in principle, a way to approach the *full CI* limit. In practise, this is not feasible in most cases. For the BH molecule with an inactive core orbital, this limit can be reached: due to the small number of electrons, very large active spaces can be used. When correlating all six electrons, the calculations become much more expensive, but approaching the limit should be possible using today's most powerful computers. This has not been done in the calculations which are reported here, but it has become obvious that including the 1σ orbital in the active space does not have a large effect on the magnetic properties studied here. Thus, the result obtained in the first series of calculations (Table 1) should be quite reliable.

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