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Magnetic Susceptibility of the BH Molecule*

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The coupled Hartree–Fock (CHF) perturbation approach and its extension to multiconfiguration wavefunctions (MC CHF scheme) were used to calculate the magnetic susceptibility of the BH molecule. The results obtained for an SCF and two pair-excitation MC SCF functions confirm the paramagnetism of the BH molecule and indicate a rather weak dependence of the computed molecular susceptibility on the correlation effects.

Key words: BH, magnetic susceptibility of ~

1. Introduction

Atomic and molecular second-order properties, such as electric polarizability or magnetic susceptibility, are often calculated within the so-called Coupled Hartree–Fock (CHF) perturbation scheme [1, 2]. There are many advantages of the CHF approach, thus: it can be used for a wide range of properties [2] and it circumvents the sum-over-states approximation, as in the computations one needs to know only the wavefunction of a given atomic or molecular state and the virtual orbitals. Finally, if the CHF calculation requires too much numerical effort one can easily introduce further simplifying approximations [3]. However, as the CHF scheme corresponds to the Hartree–Fock approach for the perturbed system it becomes unreliable for systems which have to be described using many-determinant wavefunctions.

To estimate the role of the correlation corrections to second-order properties one can use an extension of the CHF approach. We have proposed such an extension

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for multiconfiguration self-consistent field (MC SCF) functions [4, 5]. The equations of this scheme for a MC SCF function including only pair diagonal excitations [6] were discussed in detail in Ref. [4]. It seems that in this approach, which we call MC CHF perturbation scheme, all the advantages of the CHF are retained and one can additionally analyse the correlation dependence of molecular properties.

As a numerical example we have chosen the magnetic susceptibility of the boron hydride (BH) molecule. There are two reasons for this choice – first, according to the CHF calculations, BH should be paramagnetic [1, 7, 8]. Although in principle a closed-shell molecule can be paramagnetic [9, 10] this is an exceptional result. The CHF calculation of Hegstrom and Lipscomb [8] was performed using an extended STO basis set and the results are almost gauge-invariant, thus they provide a reliable reference for the other computations. The second reason is that there are many correlated wavefunctions for the ground state of BH (see Ref. [11] and references therein). Therefore, it is also possible to compare a MC SCF function with other wavefunctions used to discuss correlation effects. However, to our knowledge, the correlated wavefunctions were used to analyse the first-order properties of BH only, and except for the qualitative discussion given in [8] there is no estimate of the influence of correlation on the magnetic susceptibility of BH. As this molecule has a π orbital of low energy, this influence could be of some significance.

2. The SCF and MC SCF Wavefunctions

All the calculations were performed using the same CGTO basis set. More polarization functions were included than would be used to obtain an energy-optimized basis, as the second-order properties depend strongly on the virtual orbitals. There are some criteria to check the usefulness of a basis set, such as gauge invariance of the results or completeness of the set with respect to a given perturbing operator [12], but in this case we were interested in recovering simultaneously a significant part of the correlation energy.

The basis set was composed of $11s$, $7p$ and $1d$ orbitals on the B atom and $6s$ and $6p$ on the H atom, contracted to a (6, 4, 1/3, 2) CGTO basis. The exponents and contraction coefficients for boron s, p and hydrogen s orbitals were taken from Refs. [13, 14], the polarization functions were chosen by comparison with expansions of STO's [3, 15].

The resulting SCF wavefunction gives the total energy of -25.12798 a.u., which is close to the estimated Hartree–Fock limit (-25.1314 a.u., [16]) and compares favourably with other calculations using basis sets of this quality [11]. The dipole moment, 1.769 D, is also similar to the value of Saunders and Guest [11], i.e. 1.778 D for a 43 STO basis. This indicates appropriate choice of the polarization functions.

Using the MC SCF scheme in the approach proposed by Wood and Veillard [17] we obtained four different wavefunctions. They included in the second set (the

set of weakly occupied orbitals) respectively: one σ and one π (i.e. one π_x and one π_y orbitals), one σ and two π, two σ and two π and three σ and two π orbitals. The corresponding correlation energies were (in a.u.) 0.052, 0.060, 0.070 and 0.074, while the best configuration interaction result [18] is 0.1332 a.u. Two of our functions were not used in further calculations; the first, as an analysis of the CI coefficients shows that one π orbital does not correlate simultaneously the 2σ and 3σ core orbitals; and the third, as being very similar to the fourth. The MC SCF functions chosen finally for the calculations of the properties of BH are described in Table 1. The analysis of the CI coefficients indicates that the 3σ (lone pair) orbital is correlated mainly by 1π, the 2σ (bond) by 4σ and 2π and the 1σ (boron $1s$) – by 5σ orbital. The corresponding contributions to the correlation energy are in agreement with the results of [11].

Table 1. The SCF and MC SCF wavefunctions and the computed one-electron properties

Wave function	SCF	MC-I	MC-II
E_{tot} [a]	−25.128	−25.188	−25.202
$P(i)$ [b]			
1σ	2.0	2.000	1.999
2σ	2.0	1.978	1.979
3σ	2.0	1.877	1.880
4σ	—	0.015	0.014
$1\pi_x = 1\pi_y$	—	0.061	0.056
$2\pi_x = 2\pi_y$	—	0.004	0.004
5σ	—	—	0.001
6σ	—	—	0.008
μ [c]	1.769	1.373	1.487
χ^d(B) [d]	−18.199	−17.751	−17.904
χ^d(H) [d]	−38.061	−37.039	−36.358

[a] Total energy in atomic units.
[b] Orbital occupation numbers.
[c] Dipole moment in Debye.
[d] Diamagnetic susceptibility in ppm–cgs, the gauge origin at the atom in the brackets.

For a comparison also a CI calculation using all single and double excitations was performed. The correlation energy obtained is 0.102 a.u. and the total energy is −25.2304 a.u. The quoted earlier CI result [18] yields −25.2621 a.u., and the estimate of the correlation energy from the experimental value of −25.289 a.u. is 0.155 a.u. [19]. The results of our CI computations were used to obtain the natural orbitals. Their occupation numbers are in good agreement with the occupation numbers for the MC SCF functions and with another CI calculation [20].

3. The CHF Results

Using the SCF wavefunction we have done a standard CHF calculation of the magnetic susceptibility, χ, for gauge origin of the vector potential of the magnetic field at the B atom and at the H atom. The results are compared with those of Hegstrom and Lipscomb [8] in Table 2. The diamagnetic susceptibility, χ^d, is in good agreement with reference values for both gauge origins. However, in our calculations the total value of χ has a stronger gauge dependence due to a difference in χ^p(H). Although in our basis set the number of virtual orbitals is not

sufficient to guarantee gauge invariance the error does not seem to be very important. It is anyhow usually assumed that the value of χ calculated with the gauge origin nearer to the electronic centroid (minimum of χ^p) is more reliable [21]. Secondly, an analysis of the orbital contributions shows that the gauge dependence arises from an error in χ^p(H) of the first orbital (2.79 ppm–cgs in our computations, 8.31 ppm–cgs in [8]). The contribution of the first orbital to χ^p(B) is 0.0 ppm–cgs in both calculations. Thus it seems that our basis set is good enough to give a reliable value of χ, at least for the gauge origin at the B atom. Our results can also be compared with a recent calculation [22] using finite perturbation method and gauge invariant atomic orbitals.

Table 2. BH magnetic susceptibility – the CHF results (in ppm–cgs)

Gauge origin	B		H	
	This work	Ref. [8]	This work	Ref. [8]
χ^d	−18.20	−18.02	−38.06	−37.78
χ^p	36.02	36.77	51.21	56.30
χ	17.82	18.75	13.15	18.52

4. The MC CHF Results

The MC CHF calculations were performed using a modification of the approach described in Ref. [4]. It was observed that this scheme including all the excitations (i.e. an expansion of the perturbation correction to each of the orbitals into the full set of the unperturbed orbitals) leads to instability of the results. The instability indicates that the corresponding functional has a non-positive definite matrix of the second-order derivatives. The appropriate modifications are based on the neglect of some of the excitations from the weakly occupied orbitals.

The simplest way to obtain a proper functional is to neglect systematically all the excitations from the set of the weakly occupied orbitals (except the de-excitations to the strongly occupied, first set orbitals, which retain the orthonormality of the two sets). Such an approach is justified, as the contribution of each orbital to the total susceptibility is approximately proportional to the square of its occupation number. In a very similar manner in the calculation of the two-particle two-hole corrections in the time-dependent Hartree–Fock approximation one does not include the terms "square in the correlation coefficient" [23]. We shall denote in what follows by the symbol "A" the results obtained in this scheme.

Another approach is based on the elimination of only those excitations which lead to non-definiteness of the Hessian matrix (in TDHF language corresponding to negative excitation energies). Thus, e.g. for the MC-I function it was sufficient to eliminate the excitations from the highest occupied (weakly) 2π orbital to the four lowest unoccupied σ orbitals. The results of this approximation, for which we use the letter B, are better as the corresponding variational function

is more flexible (richer). This approach can be applied either by analysing the eigenvalues of the Hessian matrix, or, if the first-order perturbation equations are solved iteratively as is often done in the CHF calculations, by analysing the convergence of the iterative procedure. We have used, for computational reasons, the iterative technique.

The final results for the MC CHF magnetic susceptibilities are shown in Tables 3 and 4. As expected, they are similar for the approximations A and B and better (χ^p is determined variationally for the scheme B).

In comparison with the CHF calculation there is a significant difference in the individual orbital contributions, reflecting the change in 2σ and 3σ orbitals. It is observed that for the MC SCF functions the 2σ and 3σ orbitals ascribed to the bond and to the lone pair respectively differ from the SCF eigenvectors. Similarly an analysis of the aforementioned natural orbitals shows that the first is almost equal

Table 3. Orbital contributions to the total susceptibility χ(B), (in ppm–cgs)

Wave function	MC-II		SCF	SCF Ref. [8]
	A^a	B^a		
Orbital				
1σ	−0.22	−0.22	− 0.23	− 0.2
2σ	+6.13	+7.23	− 4.03	− 3.8
3σ	+5.95	+7.66	+22.08	+22.8
4σ	−0.06	+0.01	—	—
$1\pi_x = 1\pi_y$	−0.48	−0.64	—	—
$2\pi_x = 2\pi_y$	−0.03	−0.01	—	—
5σ	−0.00	−0.00	—	—
6σ	−0.07	+0.04	—	—

[a] For the definition of the approximations A and B see text.

Table 4. BH magnetic susceptibility – the MC CHF results (in ppm–cgs)

Gauge origin	B		H	
	MC-I	MC-II	MC-I	MC-II
χ^d	−17.75	−17.90	−37.04	−37.36
A^a				
χ^p	29.64	28.61	42.11	40.15
χ	11.89	10.71	5.07	2.79
B^a				
χ^p	32.16	31.31	46.17	45.33
χ	14.41	13.41	9.13	7.97

[a] For the definition of the approximations A and B see text.

to the 1σ SCF, but the second has an important contribution of 3σ SCF orbital and vice versa. However, the total molecular susceptibility is not affected by mixing of the orbitals if their occupation numbers are similar. Thus, the difference between the final CHF and MC CHF values is small, as the changes in the orbital contributions largely cancel each other.

The final results shown in Table 4 correspond to the wavefunctions which recover about 50 percent of the molecular correlation energy. However, poorly described is in our calculations the correlation of the boron $1s$ orbital, which does not contribute much to χ. Additionally, the correction to the CHF susceptibility depends mainly on the difference between the total σ and π orbital occupations, similar for the MC SCF functions used as for other quoted CI functions which yield a much better total energy. Therefore further improvement of the wavefunction should not significantly change the computed susceptibilities. We have assumed in this analysis that the correlation energy given by the unperturbed wavefunction provides an estimate of the quality of the computed correlation corrections to the second-order properties. Although this is a weak assumption, there seems to be no better criterion that could be applied in this case.

5. Conclusions

The exceptional paramagnetism of the BH molecule is an example of the influence of the external magnetic field on the nodal structure of the wavefunction. As shown by Hegstrom and Lipscomb [1, 8] and discussed in detail by Riess [24] and Heller and Hirschfelder [25], the intersection of the nodal manifolds of the real (unperturbed) part of the orbital and the imaginary (first-order perturbed) part yields the vortex line of the paramagnetic current. The effect is most important for the 3σ orbital.

For a correlated wavefunction such an analysis seems to be much more complicated. First, a nodal manifold in an orbital does not necessarily imply a node in the total wavefunction. Secondly, the dia- and paramagnetic contributions of each orbital are weighed by the occupation numbers. Finally, what is perhaps most important, the symmetry restriction (σ basis for the unperturbed, π for the first-order perturbed orbitals) is relieved in our calculations. Due to all these effects one cannot expect any quantitative results from an analysis at the MC CHF level of the induced orbital currents. The numerical results show that the qualitative reasoning performed for the CHF approximation remains valid for the correlated wavefunction. Although for the MC SCF functions the orbital picture is modified it does not change significantly the paramagnetism of the molecule.

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