

Can Induced Orbital Paramagnetism Be Controlled by Strong Magnetic Fields?

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Abstract: Magnetic hypersusceptibilities and hypershielding at the nuclei of BH, CH⁺, C₄H₄, and C₈H₈ molecules in the presence of an external spatially uniform, time-independent magnetic field have been investigated accounting for cubic response contributions via Rayleigh–Schrödinger perturbation theory. Numerical estimates have been obtained at the coupled Hartree–Fock and density-functional levels of theory within the conventional common-origin approach, using extended gaugeless basis sets. The fundamental role of electron correlation effects was assessed. Critical values of the applied magnetic field at which transition from paramagnetic to diamagnetic behavior would occur were estimated. It is shown that perturbative methods may successfully be employed to estimate the interaction energy for big cyclic molecules.

I. Introduction

Strong magnetic fields are well-known to severely modify the structure and properties of matter. This holds not only for bulk systems where extraordinary phenomena such as, for example, the quantum Hall effect, have been discovered but, in particular, for the elementary constituents of matter, that is, atoms and molecules.¹

Recently, the response of atoms and molecules to strong magnetic fields became a subject of increasing interest in different areas of physics such as astrophysics and atomic, molecular, and solid-state physics. Bound-particle systems in external magnetic fields show a number of intriguing features which are not observable in field-free space and which manifest themselves at the level of the basic equations of motion.

Observations of radio pulsars and accreting neutron stars in X-ray binaries, possessing surface fields in excess of 10⁸ T, and the detection of magnetic white dwarf stars with superstrong fields have further increased interest in this area. A “magnetar” with a magnetic field stronger than any other

known object in the universe, the soft gamma repeater known as SGR 1900+14, lying 20 000 light years away, has been discovered in the constellation of Aquila.² Magnetic fields as big as 800 trillion times that of the Earth cause the surface of magnetars to ripple and crack, releasing strong bursts of radiation.

A review of atoms in strong magnetic fields, reporting tabulations of numerical data, is available in a monograph by Ruder et al.³ Other references are the conference proceedings on *Atoms and Molecules in Strong External Fields* edited by Schmelcher and Schweizer⁴ and the special issue of the *International Journal of Quantum Chemistry* dedicated to the properties of molecules in strong magnetic fields, edited by Runge and Sabin.⁵ An extensive review on atoms, molecules, and bulk matter has been reported by Lai.¹

Atoms and molecules in strong magnetic fields are also of interest from a purely theoretical point of view.^{6,7} The difficulty in theoretically treating atoms in strong magnetic fields lies in the fact that a strong rearrangement of the electronic wave function takes place, which is particularly dramatic in the so-called intermediate regime, in which matter interacts with fields from 10³ to 10⁵ T. In the presence of fields of this strength, magnetic and Coulomb forces are of nearly equal importance: neither can be treated as a

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perturbation of the other. Due to the competition of the spherically symmetric Coulomb potential, and the cylindrically symmetric magnetic field interaction, the problem is formally non-integrable.

The “strong field” regime is typical of a situation in which the Lorentz force is on the order of magnitude of or greater than the Coulomb binding force. For a hydrogen atom in the ground state, the corresponding field strength cannot be reached in the laboratory, but only in astrophysical objects. However, the strong magnetic field regime is accessible in the laboratory for highly excited Rydberg states of atoms.^{3,4,8}

In molecules, difficulties arise from nonseparability of the center of mass and internal motion,⁷ and the screened Born–Oppenheimer approximation^{6,9} has been advocated to guarantee the validity of an adiabatic approximation in the presence of magnetic fields. Most studies of molecules in strong magnetic fields have been restricted to hydrogen molecular ion H_2^+ .^{10–16} There exist some investigations dealing with the electronic structure of the neutral molecule H_2 in the presence of a strong magnetic field.^{17–23}

Highly excited states of H_2 were studied for a field strength of 4.7 T by Monteiro and Taylor.¹⁷ For intermediate field strengths, two studies of almost qualitative character examined the potential energy curve of the lowest $^1\Sigma_g$ state.^{18,19} A few investigations were performed at the high field limit,^{20–24} where the magnetic forces dominate over the

Coulomb forces. The ground state of the H_2 molecule in the parallel configuration, in which the internuclear and magnetic field axes coincide, has been investigated by Kravchenko and Liberman,^{25,26} and by Detmer et al.^{25,27,28}

According to the fundamental results arrived at in ref 26 using a fully numerical Hartree–Fock approach, the ground state of H_2 in a magnetic field below 4.2×10^4 T is the strongly bound singlet state $^1\Sigma_g$. For magnetic fields stronger than 3×10^6 T, the ground state becomes the strongly bound triplet $^3\Pi_u$, and for magnetic fields between 4.2×10^4 T and 3×10^6 T, the symmetry of the ground state is the triplet state $^3\Sigma_u$, which is characterized by repulsion at intermediate internuclear distances and by a weak quadrupole–quadrupole interaction between atoms at large internuclear separation. In this region of magnetic field strength, the hydrogen molecule is bound weakly, if at all; the hydrogen atoms behave like a weakly nonideal gas of Bose particles and can form a superfluid phase.

Nonperturbative Hartree–Fock calculations on molecules in strong magnetic fields were recently reported using London orbitals by Tellgren et al. For a number of molecules, plots of the interaction energy as a function of the magnetic field were shown.^{29,30} Highly nonlinear behavior was discovered for closed-shell paramagnetic species BH and CH^+ , which would become diamagnetic for field strengths higher than 0.22 and 0.45 au, respectively. Surprisingly

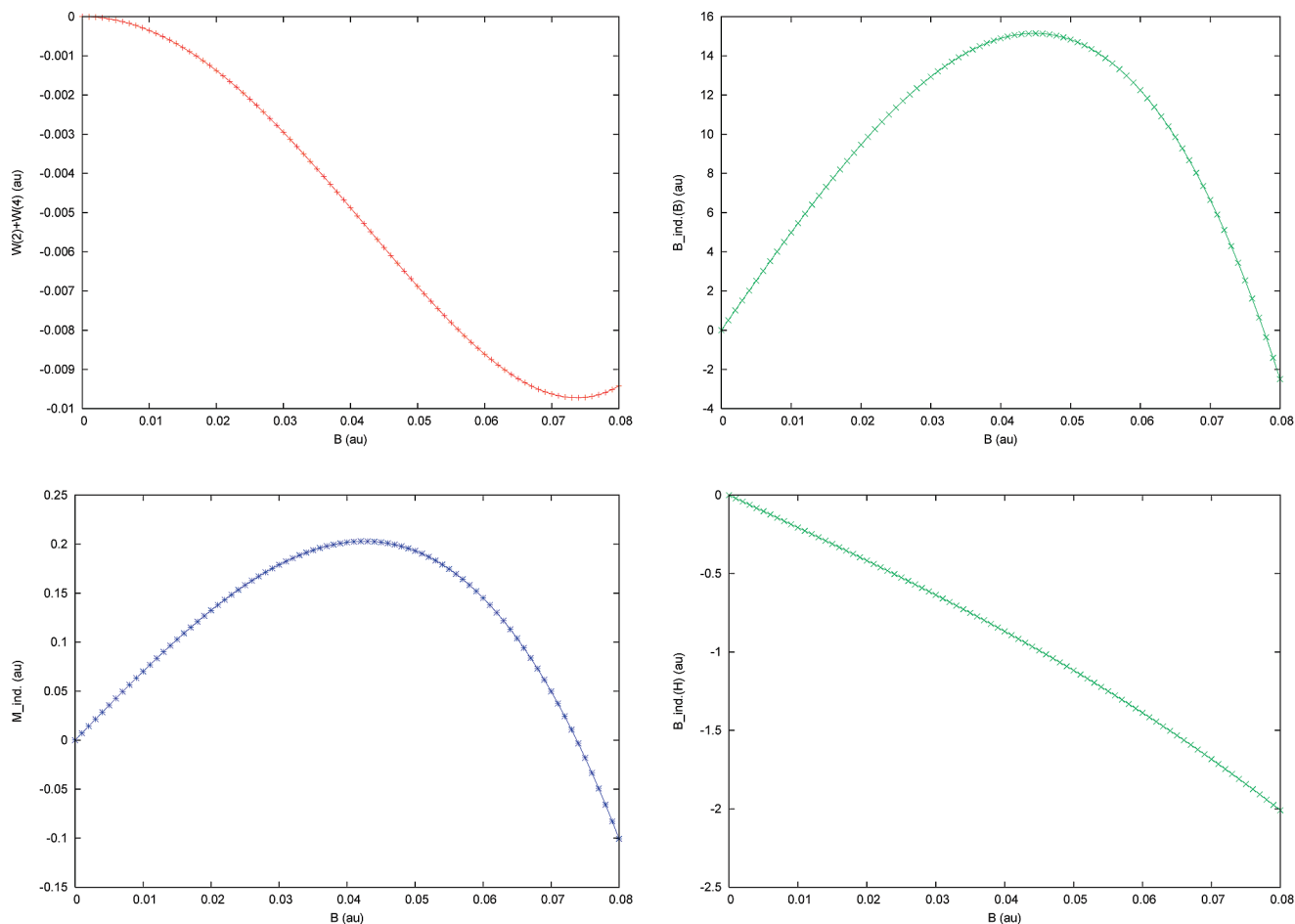


Figure 1. Response properties of the BH molecule in a magnetic field normal to the bond direction. Top left: Magnetic interaction energy. Top right: Magnetic field induced at the boron nucleus. Bottom left: Induced magnetic moment. Bottom right: Magnetic field induced at the hydrogen nucleus.

Table 1. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^B$, and Shielding, $\sigma_{\alpha\beta}^B$, of the Boron Nucleus in the BH Molecule

method	component ^c	$\Sigma^B(B)^d$	$\Sigma^B(H)^d$
CHF (CO)	xxxx	5.043×10^5	5.043×10^5
	xyxy	1.681×10^5	1.681×10^5
	xxzz	-3.009×10^4	-3.009×10^4
	zxxz	-3.600×10^4	-3.600×10^4
	zzzz	45.0	45.0
	$\langle \Sigma^B \rangle$	2.425×10^5	2.425×10^5
DFT (KT3)	xxxx	3.808×10^5	4.252×10^5
	xyxy	1.269×10^5	1.417×10^5
	xxzz	-2.143×10^4	-2.143×10^4
	zxxz	-2.572×10^4	-2.572×10^4
	zzzz	47.89	47.89
	$\langle \Sigma^B \rangle$	1.843×10^5	2.079×10^5

method	CHF(CO)	DFT(KT3)
component ^e	$\sigma^B(B)^d$	$\sigma^B(B)^d$
xx	-506.7	-398.7
zz	198.9	202.4
$\langle \sigma^B \rangle$	-271.5	-198.3
component	$\sigma^B(H)^d$	$\sigma^B(H)^d$
xx	-506.6	-398.6
zz	198.9	202.4
$\langle \sigma^B \rangle$	-271.5	-198.3

^a In ppm SI atomic units. The conversion factor to SI units is $1.80997698 \times 10^{-11} \text{ T}^{-2}$, using the CODATA values of the fundamental constants 2002.⁸³ Coordinates in bohr: H (0, 0, -2.1120108509); B (0, 0, 0.19333975910). ^b In ppm. ^c Only components contributing to the average property are reported. $yyyy = xxxx$, $xyxy = yxyx$, $xxzz = yyzz$, $zxxz = zyyz$ by symmetry. ^d Common origin results; the gauge origin is indicated between parentheses. ^e $xx = yy$ by symmetry.

enough, the curve for BH in the presence of a perpendicular field indicates that, for a field as big as 0.4 au, that is, $\approx 10^5$ T, the interaction energy would vanish, as happens for the molecule in the absence of magnetic perturbation, see Figure 1d of ref 29.

II. Perturbation Theory Approach to Cubic Response

Perturbation theory, which is applicable in the weak field regime, breaks down in the intermediate field regime. However, for a time, standard perturbative methods were taken into account for predicting observable phenomena in a terrestrial environment.³¹ Ramsey³² considered possible deviations from linear dependence of the resonance frequencies on the strength of the external magnetic field in nuclear magnetic resonance (NMR) spectroscopy. Bendall and Dordrell reported an experimental observation of a field-dependent ⁵⁹Co chemical shift in two compounds.³¹ Žaucer and Ažman³³ suggested that departures from linear dependence between the induced magnetic dipole moment and the applied field can arise in a molecule, due to magnetic field dependence of the magnetic susceptibility. Magnetic field-dependent nuclear spin–spin coupling was discussed by Raynes and Stevens via fourth-order perturbation theory.³⁴

A few semiempirical^{35,36} and ab initio calculations³⁷ have been carried out. Theoretical aspects of the magnetic-field dependence of quadrupole splitting in ¹³¹Xe were considered by Vaara and Pykkö, who presented accurate numerical predictions³⁸ in good agreement with corresponding experi-

Table 2. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^H$, and Shielding, $\sigma_{\alpha\beta}^H$, of the Hydrogen Nucleus in the BH Molecule^a

method	component	$\Sigma^H(H)$	$\Sigma^H(B)$
CHF (CO)	xxxx	4252	4242
	xyxy	1417	1414
	xxzz	-277.6	-277.7
	zxxz	-4299	-4298
	zzzz	24.55	24.55
	$\langle \Sigma^H \rangle$	442.1	436.8
DFT (KT3)	xxxx	7857	5898
	xyxy	2619	1966
	xxzz	-350.1	-350.2
	zxxz	-3081	-3082
	zzzz	27.90	27.90
	$\langle \Sigma^H \rangle$	2823	1778

method	CHF(CO)	DFT(KT3)
component	$\sigma^H(H)$	$\sigma^H(H)$
xx	20.58	18.25
zz	33.93	34.18
$\langle \sigma^H \rangle$	25.03	23.56
component	$\sigma^H(B)$	$\sigma^H(B)$
xx	20.56	18.23
zz	33.93	34.10
$\langle \sigma^H \rangle$	25.02	23.55

^a See footnotes a–e of Table 1 for the use of symbols, units, and abbreviations.

mental values.³⁹ Theoretical and computational studies on nuclear magnetic shielding in closed-shell atoms as a function of even powers of a perturbing magnetic field were reported by Vaara and co-workers,⁴⁰ and the magnetic-field dependence of ⁵⁹Co nuclear magnetic shielding in Co(III) complexes was investigated.⁴¹ Nonlinear ring currents and the effect of strong magnetic fields on π -electron circulation were analyzed by Soncini and Fowler.⁴²

Increasing attention is being paid to nonlinear magnetic response⁴³ in view of possible technological applications, for example, a semiconductor-to-metal switch, which can be operated via the Aharonov-Bohm effect in carbon nanocylinders whose axes are aligned along a strong magnetic field,^{44,45} the quantum Hall effect observed in graphene sheets at room temperature,⁴⁶ and the field-induced change of the electronic band structure of CeBiPt evidenced by electrical-transport measurements in pulsed magnetic fields.⁴⁷

A systematic study of molecular response to intense magnetic fields in the lower limit of the intermediate regime has recently been undertaken to rationalize the phenomenology induced in the electron distribution of diamagnetic atoms and molecules: a computational approach to nonlinear magnetic field dependence of magnetic susceptibility and electric and magnetic nuclear shielding has been developed in a series of papers within the framework of the Rayleigh–Schrödinger perturbation theory, allowing for the conventional common origin (CO) choice, gaugeless basis sets, and coupled Hartree–Fock approximation.^{48–55}

The present study attempts to evaluate fourth-rank hypermagnetizability and nuclear magnetic hypershielding tensors in some closed-shell systems characterized by induced orbital paramagnetism,⁵⁶ the BH molecule,^{56–69} the CH⁺ cation,^{68–70} and two planar unsaturated hydrocarbons exhibiting π paramagnetism, cyclobutadiene C₄H₄,^{71,72} and flattened cy-

Table 3. Magnetic Hypersusceptibility,^a $\chi_{\alpha\beta\gamma\delta}$, and Susceptibility,^b $\chi_{\alpha\beta}$, of the BH Molecule

method	component ^c	$\chi(H)^d$	$\chi(CM)^d$
CHF (CO)	xxxx	-7882	-7881
	xxyy	-2627	-2627
	xxzz	400.2	400.2
	zzzz	36.02	36.02
	$\langle\chi\rangle$	-3876	-3875
DFT (KT3)	xxxx	-6962	-5902
	xxyy	-2320	-1967
	xxzz	277.8	277.9
	zzzz	41.28	41.28
	$\langle\chi\rangle$	-3483	-2918

method	CHF(CO)	DFT(KT3)
component ^e	$\chi(H)^d$	$\chi(H)^d$
xx	7.15	5.44
zz	-2.51	-2.50
$\langle\chi\rangle$	3.93	2.80
component ^e	$\chi(CM)^d$	$\chi(CM)^d$
xx	7.15	5.44
zz	-2.51	-2.50
$\langle\chi\rangle$	3.93	2.79

^a In SI atomic units. The conversion factor to SI units is $1.42825951 \times 10^{-39}$ JT⁻⁴ per molecule, see ref 83. ^b In SI atomic units. The conversion factor to SI units is $7.89103660 \times 10^{-29}$ JT⁻², see ref 83. ^c Only components contributing to the average property are reported. yyy = xxx and xxzz = yzzz by symmetry. ^d Common origin results; the gauge origin is indicated between parentheses. ^e xx = yy by symmetry.

Table 4. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^C$, and Shielding, $\sigma_{\alpha\beta}^C$, of the Carbon Nucleus in the CH⁺ Cation^a

method	component	$\Sigma^C(C)$	$\Sigma^C(H)$
CHF (CO)	xxxx	2.642×10^6	2.618×10^6
	xxyy	8.807×10^5	8.727×10^5
	xxzz	-1.103×10^5	-1.095×10^5
	zxxz	-1.307×10^5	-1.297×10^5
	zzzz	14.99	14.99
	$\langle\Sigma^C\rangle$	1.313×10^6	1.301×10^6
DFT (KT3)	xxxx	8.983×10^5	9.665×10^5
	xxyy	2.994×10^5	3.222×10^5
	xxzz	-4.820×10^4	-4.821×10^4
	zxxz	-5.749×10^4	-5.750×10^4
	zzzz	15.68	15.68
	$\langle\Sigma^C\rangle$	4.368×10^5	4.732×10^5

method	CHF(CO)	DFT(KT3)
component	$\sigma^C(C)$	$\sigma^C(C)$
xx	-2051	-1276
zz	247.0	250.4
$\langle\sigma^C\rangle$	-1285	-767.0
component	$\sigma^C(H)$	$\sigma^C(H)$
xx	-2047	-1276
zz	247.0	250.4
$\langle\sigma^C\rangle$	-1282	-767.1

^a See footnotes a–e of Table 1 for the use of symbols, units, and abbreviations. Coordinates in bohr: H (0, 0, 0); C (0, 0, 2.1370912849).

clo-octatetraene (COT) C₈H₈. A “clamped” planar structure of COT is annelated with perfluorocyclobuteno moieties⁷³ and with bicyclo[2.1.1] hex-2-ene groups.^{74,75}

The scope of the present research is (i) to investigate the reliability and the limits of approaches neglecting contributions higher than a cubic response's; (ii) to

Table 5. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^H$, and Shielding, $\sigma_{\alpha\beta}^H$, of the Hydrogen Nucleus in the CH⁺ Cation^a

method	component	$\Sigma^H(H)$	$\Sigma^H(C)$
CHF (CO)	xxxx	-2.032×10^4	-2.034×10^4
	xxyy	-6773	-6779
	xxzz	789.0	789.1
	zxxz	-7665	-7659
	zzzz	5.86	5.86
DFT (KT3)	$\langle\Sigma^H\rangle$	-1.359×10^4	-1.359×10^4
	xxxx	-4295	-4966
	xxyy	-1432	-1655
	xxzz	231.9	232.0
	zxxz	-3320	-3317
zzzz	7.42	7.42	
$\langle\Sigma^H\rangle$	-3525	-3881	

method	CHF(CO)	DFT(KT3)
component	$\sigma^H(H)$	$\sigma^H(H)$
xx	35.79	27.63
zz	30.17	30.56
$\langle\sigma^C\rangle$	33.92	28.61
component	$\sigma^H(C)$	$\sigma^H(C)$
xx	35.65	27.50
zz	30.17	30.56
$\langle\sigma^H\rangle$	33.82	28.52

^a See footnotes a–e of Table 1 for the use of symbols, units, and abbreviations.

compare fourth-rank hypermagnetizabilities and hyper-shieldings as properties suitable for experimental detection of nonlinear behavior; (iii) to estimate the contribution of electron correlation to fourth-rank magnetic tensors via density functional theory (DFT), allowing for the Keal-Tozer KT3 functional;^{76,77} and (iv) to investigate whether induced orbital paramagnetism can be controlled by applying a magnetic field of increasing strength.

The approaches employed are outlined in section III. Numerical estimates of the fourth-rank hypershieldings for the molecules BH, C₄H₄, and C₈H₈ and the CH⁺ cation, and a discussion of results are also reported in section III.

III. Calculation of Fourth-Rank Magnetic Tensors

The energy of a closed-shell molecule in the electronic reference state *a*, in the presence of an external spatially uniform and time-independent magnetic field **B** and of an intramolecular permanent magnetic dipole *m_I* at nucleus *I* can be written as a Taylor series:^{48–55}

$$W_a = W_a^{(0)} + W_a^{(2)} + W_a^{(4)} + \dots = W_a^{(0)} - \frac{1}{2} \chi_{\alpha\beta} B_\alpha B_\beta - \frac{1}{24} \chi_{\alpha\beta\gamma\delta} B_\alpha B_\beta B_\gamma B_\delta + \dots + \sigma_{\alpha\beta}^I m_{I\alpha} B_\beta + \frac{1}{6} \Sigma_{\alpha\beta\gamma\delta}^I m_{I\alpha} B_\beta B_\gamma B_\delta + \dots \quad (1)$$

where $W_a^{(0)}$ is the energy of the isolated molecule, $\chi_{\alpha\beta}$ is the magnetic susceptibility, and $\sigma_{\alpha\beta}^I$ is the magnetic shielding at nucleus *I*. The fourth-rank tensors $\chi_{\alpha\beta\gamma\delta}$ and $\Sigma_{\alpha\beta\gamma\delta}^I$ account for nonlinear response in **B**. The explicit expressions needed to calculate these quantities contain 10 propagators, see eq 18 of ref 48 and eq 28 of ref 53. Einstein's convention of summing over repeated Greek indices is in force throughout this paper.

Table 6. Magnetic Hypersusceptibility,^a $\chi_{\alpha\beta\gamma\delta}$, and Susceptibility, $\chi_{\alpha\beta}$, of the CH⁺ Cation

Method	Component	X (H)	X (CM)
CHF (CO)	xxxx	-1.452×10^4	-1.451×10^4
	xyyy	-4839	-4836
	xxzz	574.2	573.8
	zzzz	4.57	4.57
	$\langle X \rangle$	-7282	-7279
DFT (KT3) ^c	xxxx	-5435	-4880
	xyyy	-1812	-1627
	xxzz	242.8	242.5
	zzzz	4.79	4.79
	$\langle X \rangle$	-2703	-2408

method	CHF(CO)	DFT(KT3)
component	$\chi(H)$	$\chi(H)$
xx	10.59	6.30
zz	-1.44	-1.44
$\langle \chi \rangle$	6.58	3.72
component	$\chi(CM)$	$\chi(CM)$
xx	10.59	6.29
zz	-1.44	-1.44
$\langle \chi \rangle$	6.58	3.72

^a See footnotes a–e of Table 3 for the use of symbols, units, and abbreviations.

The induced orbital magnetic dipole is

$$\langle \hat{m}_\alpha \rangle = -\frac{\partial W_a}{\partial B_\alpha} = \chi_{\alpha\beta} B_\beta + \frac{1}{6} X_{\alpha\beta\gamma\delta} B_\beta B_\gamma B_\delta + \dots - \sigma_{\beta\alpha}^J m_{I\beta} - \frac{1}{2} \sum_{\beta\alpha\gamma\delta}^J m_{I\beta} B_\gamma B_\delta + \dots \quad (2)$$

The magnetic field induced at the nucleus in question by the n electrons responding to the perturbation is

$$\langle \hat{B}_{I\alpha}^n \rangle = -\frac{\partial W_a}{\partial m_{I\alpha}} = -\sigma_{\alpha\beta}^J B_\beta - \frac{1}{6} \sum_{\alpha\beta\gamma\delta}^J B_\beta B_\gamma B_\delta + \dots = - \int \sigma_{\alpha\beta}^J(\mathbf{B}) dB_\beta \quad (3)$$

where

$$\sigma_{\alpha\beta}^J(\mathbf{B}) = \sigma_{\alpha\beta}^J + \frac{1}{2} \sum_{\alpha\beta\gamma\delta}^J B_\gamma B_\delta + \dots \quad (4)$$

is the field-dependent magnetic shielding at nucleus I . For the species BH and CH⁺ characterized by diamagnetism in the z bond direction, that is, $\chi_{ll} \equiv \chi_{zz} < 0$, and strong paramagnetism in the radial direction, we will consider only terms depending on B_\perp , rewriting eq 1 in the truncated form

$$W_a - W_a^{(0)} \approx W_a^{(2)} + W_a^{(4)} \approx -\frac{1}{2} \chi_\perp B_\perp^2 + \frac{1}{24} |X_\perp| B_\perp^4 \quad (5)$$

where the perpendicular components of the susceptibility are denoted $\chi_\perp \equiv \chi_{xx} = \chi_{yy} > 0$ and $X_\perp \equiv X_{xxxx} = X_{yyyy} < 0$. The interaction energy (eq 5) has a local maximum $W_a^{(2)} + W_a^{(4)} = 0$ for $B_\perp = 0$, an inflection point for $B_\perp \equiv B_s = \sqrt{(2\chi_\perp/|X_\perp|)}$, a minimum $-3\chi_\perp^2/(2|X_\perp|)$ for $B_\perp \equiv B_m = \sqrt{(6\chi_\perp/|X_\perp|)}$. It vanishes also for $B_\perp \equiv B_c = \sqrt{(12\chi_\perp/|X_\perp|)}$, and it becomes positive, that is, destabilizing, beyond this field value.

The orbital magnetic dipole induced by B_\perp in the radial direction of the BH molecule

$$\langle \hat{m}_\perp \rangle = \chi_\perp B_\perp + \frac{1}{6} X_\perp B_\perp^3 + \dots \quad (6)$$

reaches its maximum paramagnetic value $\langle m_s \rangle = (2/3)\chi_\perp \sqrt{(2\chi_\perp/|X_\perp|)}$ at the inflection point of the interaction energy, B_s . It vanishes at $B_\perp = 0$ and for $B_\perp = B_m$, where transition from paramagnetic to diamagnetic response occurs. For instance, using the theoretical CHF results reported in Table 3, $\chi_\perp = 7.15$ au and $X_\perp = -7882$ au, we find $B_s \approx 4.3 \times 10^{-2}$ au and $\langle m_s \rangle \approx 0.20$ au, compare Figure 1.

The radial component of magnetic field induced at nucleus I by B_\perp applied perpendicular to the BH bond is

$$\langle \hat{B}_{I\perp}^n \rangle = -\sigma_\perp^J B_\perp - \frac{1}{6} \sum_\perp^J B_\perp^3 + \dots \quad (7)$$

indicating by σ_\perp^J and \sum_\perp^J the perpendicular components of nuclear shielding and hypershielding. If I is either H or B, with σ_\perp^J and \sum_\perp^J of opposite sign, then an extremum point of $\langle \hat{B}_{I\perp}^n \rangle$ occurs at $B_\perp^* = \sqrt{(12\sigma_\perp^J/\sum_\perp^J)}$. Relationships similar to 5–7 hold for the other systems studied.

Magnetic susceptibilities and hypersusceptibilities, magnetic shielding, and hypershieldings at the nuclei have been calculated for BH, CH⁺, C₄H₄, and C₈H₈ at two levels of

Table 7. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^C$, and Shielding, $\sigma_{\alpha\beta}^C$, of the Carbon Nucleus in the C₄H₄ Molecule^a

method	component	$\Sigma^C(C)$	$\Sigma^C(CM)$
CHF (CO)	xxxx	7751	7728
	xyyy	-2727	-2719
	xxzz	-1808	-1805
	yxyy	-1.884×10^4	-1.890×10^4
	yyyy	-1900	-1863
	yyzz	916.4	893.6
	zxxz	5454	5424
	zyyz	2559	2550
	zzzz	1.252×10^4	1.250×10^4
	$\langle \Sigma^C \rangle$	785.6	761.5
	DFT (KT3)	xxxx	1.253×10^4
xyyy		-2029	-2090
xxzz		-1232	-1305
yxyy		-1.726×10^4	-1.642×10^4
yyyy		1151	1075
yyzz		1361	1405
zxxz		5831	6309
zyyz		2673	2713
zzzz		1.231×10^4	1.208×10^4
$\langle \Sigma^C \rangle$		3066	3211

method	CHF(CO)	DFT(KT3)
component	$\sigma^C(C)$	$\sigma^C(C)$
xx	124.2	108.1
yy	107.0	94.23
yz	-69.37	-56.46
zy	28.51	28.29
zz	-106.6	-66.40
$\langle \sigma^C \rangle$	41.53	45.32
component	$\sigma^C(H)$	$\sigma^C(H)$
xx	124.1	108.0
yy	106.9	94.18
yz	-69.32	-56.42
zy	28.67	28.49
zz	-106.7	-66.57
$\langle \sigma^C \rangle$	41.42	45.21

^a See footnotes a–e of Table 1 for the use of symbols, units, and abbreviations. Coordinates in bohr: H (0, 2.69820955550, 2.9255001457); C (0, 1.2552449153, 1.4870179359).

Table 8. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^H$, and Shielding, $\sigma_{\alpha\beta}^H$, of the Hydrogen Nucleus in the C_4H_4 Molecule^a

method	component	$\Sigma^H(H)$	$\Sigma^H(CM)$	
CHF (CO)	xxxx	-1410	-1493	
	xyxy	57.94	26.24	
	xxzz	55.54	31.05	
	yxyx	-941.3	-958.5	
	yyyy	-132.6	-180.9	
	yyzz	-57.33	-74.16	
	zxxz	170.6	158.2	
	zyyz	-63.49	-76.61	
	zzzz	504.5	460.6	
	$\langle\Sigma^H\rangle$	-363.3	-421.5	
	DFT (KT3)	xxxx	-907.6	-1981
		xyxy	176.7	8.86
		xxzz	132.1	17.18
yxyx		-829.0	-952.1	
yyyy		225.7	-75.79	
yyzz		43.00	-49.71	
zxxz		237.2	115.1	
zyyz		43.64	-51.34	
zzzz		720.0	475.0	
$\langle\Sigma^H\rangle$		-31.66	-498.8	

method	HF(CO)	DFT(KT3)
component	$\sigma^H(H)$	$\sigma^H(H)$
xx	28.04	28.15
yy	28.77	27.56
zz	21.21	21.90
$\langle\sigma^C\rangle$	26.00	25.87
component	$\sigma^H(CM)$	$\sigma^H(CM)$
xx	27.61	27.70
yy	28.57	27.38
zz	21.01	21.72
$\langle\sigma^H\rangle$	25.73	25.60

^a See footnotes a–e of Table 1 for the use of symbols, units, and abbreviations.

Table 9. Magnetic Hypersusceptibility, $\chi_{\alpha\beta\gamma\delta}$, and Susceptibility, $\chi_{\alpha\beta}$, of the C_4H_4 Molecule

method	component	$\chi(C)$	$\chi(CM)$	
CHF (CO)	xxxx	-3869	-3847	
	xyxy	-81.99	-72.78	
	xxzz	39.09	46.01	
	yyyy	-431.7	-405.7	
	yyzz	-41.50	-36.16	
	zzzz	-146.7	-139.5	
	$\langle\chi\rangle$	-923.3	-903.6	
	DFT (KT3)	xxxx	-5329	-4999
		xyxy	-222.6	-158.4
xxzz		-5.57	25.71	
yyyy		-563.8	-454.0	
yyzz		-85.26	-59.48	
zzzz		-223.0	-182.2	
$\langle\chi\rangle$		-1348	-1204	

method	HF(CO)	DFT(KT3)
component	$\chi(C)$	$\chi(C)$
xx	-0.78	-0.13
yy	-4.60	-4.21
zz	-5.27	-5.20
$\langle\chi\rangle$	-3.55	-3.18
component	$\chi(CM)$	$\chi(CM)$
xx	-0.77	-0.12
yy	-4.59	-4.21
zz	-5.26	-5.19
$\langle\chi\rangle$	-3.54	-3.17

^a See footnotes a–e of Table 3 for the use of symbols, units, and abbreviations.

Table 10. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^C$, and Shielding, $\sigma_{\alpha\beta}^C$, of the Carbon Nucleus in the C_8H_8 Molecule^a

method	CHF(CO)	DFT(KT3)
component	$\Sigma^C(C)$	$\Sigma^C(C)$
xxxx	7211	7883
xyxy	2249	2124
xxzz	-4.655×10^4	-8.584×10^4
yxyx	2853	2831
yyyy	4512	4597
yyzz	2.215×10^4	5.021×10^4
zxxz	1134	2526
zyyz	-835.9	-409.1
zzzz	8.016×10^4	5.561×10^4
$\langle\Sigma^C\rangle$	1.458×10^4	1.080×10^5

method	CHF(CO)	DFT(KT3)
component	$\sigma^C(C)$	$\sigma^C(C)$
xx	-2.40	-0.26
yy	24.72	36.73
zz	143.3	106.4
$\langle\sigma^C\rangle$	55.20	47.61

^a See footnotes a–e of Table 1 for the use of symbols, units, and abbreviations. Coordinates in bohr: H (5.1668362830, 2.1620413390, 0); C (3.2324200158 1.40696913683, 0).

Table 11. Magnetic Hypershielding, $\Sigma_{\alpha\beta\gamma\delta}^H$, and Shielding, $\sigma_{\alpha\beta}^H$, of the Hydrogen Nucleus in the C_8H_8 Molecule^a

Method	CHF(CO)	DFT(KT3)
component	$\Sigma^H(H)$	$\Sigma^H(H)$
xxxx	446.9	762.7
xyxy	122.1	308.9
xxzz	-1440	-2473
yxyx	66.00	250.0
yyyy	42.0	888.1
yyzz	503.3	1981
zxxz	72.75	195.2
zzzz	-3.323×10^4	-2.033×10^5
$\langle\Sigma^H\rangle$	-6.690×10^3	-4.029×10^4

method	CHF(CO)	DFT(KT3)
component	$\sigma^H(H)$	$\sigma^H(H)$
xx	27.94	27.17
yy	30.63	30.29
zz	33.12	41.03
$\langle\sigma^H\rangle$	30.56	32.83

^a See footnotes a–e of Table 1 for the use of symbols, units, and abbreviations.

Table 12. Magnetic Hypersusceptibility, $\chi_{\alpha\beta\gamma\delta}$, and Susceptibility, $\chi_{\alpha\beta}$, of the C_8H_8 Molecule

method	CHF(CO)	DFT(KT3)
component	$\chi(CM)$	$\chi(CM)$
xxxx	-477.1	-818.7
xyxy	-166.1	-303.8
xxzz	-554.5	-1459
zzzz	-1.393×10^5	-8.492×10^5
$\langle\chi\rangle$	-2.857×10^4	-1.715×10^5

method	CHF(CO)	DFT(KT3)
component	$\chi(CM)$	$\chi(CM)$
xx	-12.25	-11.34
zz	16.78	48.83
$\langle\chi\rangle$	-2.57	8.72

^a See footnotes a–e of Table 3 for the use of symbols, units, and abbreviations.

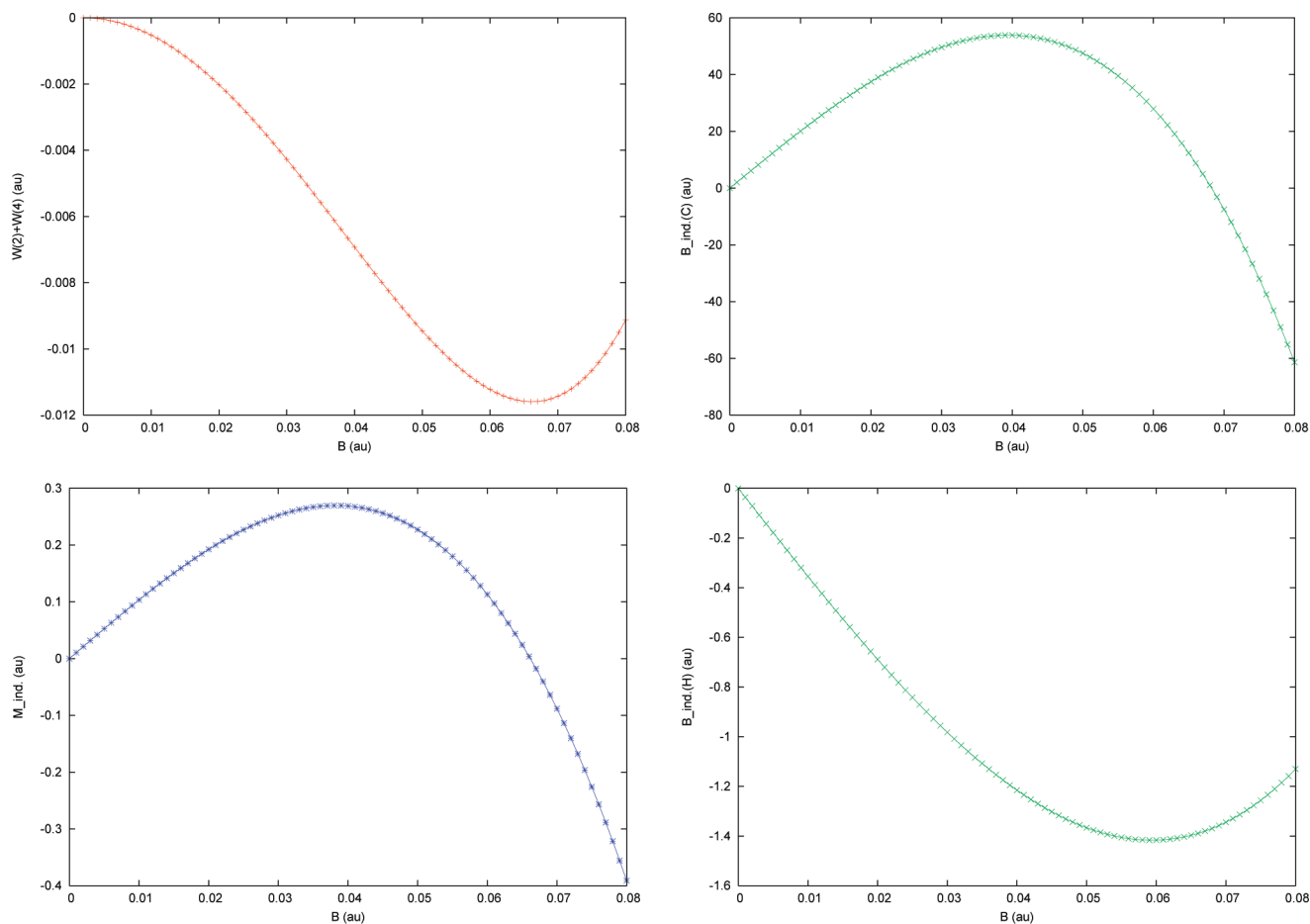


Figure 2. Response properties of the CH^+ cation in a magnetic field normal to the bond direction. Top left: Magnetic interaction energy. Top right: Magnetic field induced at the carbon nucleus. Bottom left: Induced magnetic moment. Bottom right: Magnetic field induced at the hydrogen nucleus.

accuracy, coupled Hartree–Fock (CHF), equivalent to random-phase approximation (RPA), and DFT, allowing for the KT3 functional,^{76,77} implemented in the DALTON package.⁷⁸ The KT3 functional was found to be the most efficient for calculating shielding constants in a series of small molecules⁷⁹ and for studies of hydrogen bonding.⁸⁰ Calculated values for tensor components are reported in Tables 1–12. The isotropic term $\langle \Sigma^I \rangle$ is defined:

$$\langle \Sigma \rangle^I = \frac{1}{15} [\Sigma'_{\alpha\alpha\beta\beta} + \Sigma'_{\alpha\beta\alpha\beta} + \Sigma'_{\alpha\beta\beta\alpha}] \quad (8)$$

and $\langle X \rangle$ is analogously defined.

We give data needed to reproduce our calculations of the properties in eqs 1–7. Gaussian basis sets used for the BH molecule are as follows: for B, the 13s set from ref 81 plus one s with exponent 0.022845; the 8p set from ref 81 plus a 3p set of functions with exponents 880.0, 220.0, and 0.01588267; the 8d set with exponents 29.97, 9.99, 3.33, 1.110, 0.402, 0.145, 0.048333, and 0.016111; the 5f set with exponents 2.646, 0.882, 0.311, 0.103667, and 0.03455567; for H, the 10s set from ref 81; the 6p set with exponents 18.807, 6.269, 2.292, 0.838, 0.292, and 0.09733; the 3d set with exponents 3.171, 1.057, and 0.3523. Gaussian basis sets used for the CH^+ and C_4H_4 molecules are as follows: for C, the 13s set from ref 81, the 8p set from ref 81 plus a 2p set of functions with exponents 1512.9 and 355.1; the 5d set

with exponents 5.262, 1.848, 0.649, 0.228, and 0.08; and the 2f set with exponents 1.419 and 0.485; for H, the 10s set from ref 81, the 4p set with exponents 6.269, 2.292, 0.838, and 0.292; one d function with exponent 1.057. The Gaussian basis set used for the C_8H_8 molecule was the truncated aug-cc-pCVTZ, (12s7p3d2f/6s3p2d) \rightarrow 6s5p3d2f/4s3p2d basis set from ref 52. The molecular geometries for BH, and CH^+ were optimized at the HF scheme with the same basis set employed in the calculations; that of C_4H_4 was optimized at the B3LYP⁸² level of theory, with the same basis set employed in the calculations. The molecular geometry of cyclo-octatetraene was taken from ref 52. The interaction energy, eq 5; induced orbital magnetic moment, eq 6; and magnetic field induced at the nuclei, eq 7, are displayed in Figures 1–4 as a function of the applied magnetic field.

Within the assumption of cubic response, the values of magnetic field $B_{\perp} = B_m$ at which a transition from the paramagnetic to diamagnetic response would take place (corresponding to a change of sign in eq 6 for the induced moment) are, in atomic units (1 au of magnetic flux density $\hbar/ea_0^2 = 2.35051742 \times 10^5$ T from ref 83), $\approx 7.4 \times 10^{-2}$, $\approx 6.6 \times 10^{-2}$, and $\approx 2.7 \times 10^{-2}$, respectively, for BH, CH^+ , and C_8H_8 , within the CHF approximation, see the red and blue curves in Figures 1, 2, and 4. Since χ_{\perp} and X_{\perp} have the same sign in C_4H_4 , no transition was observed in Figure 3.

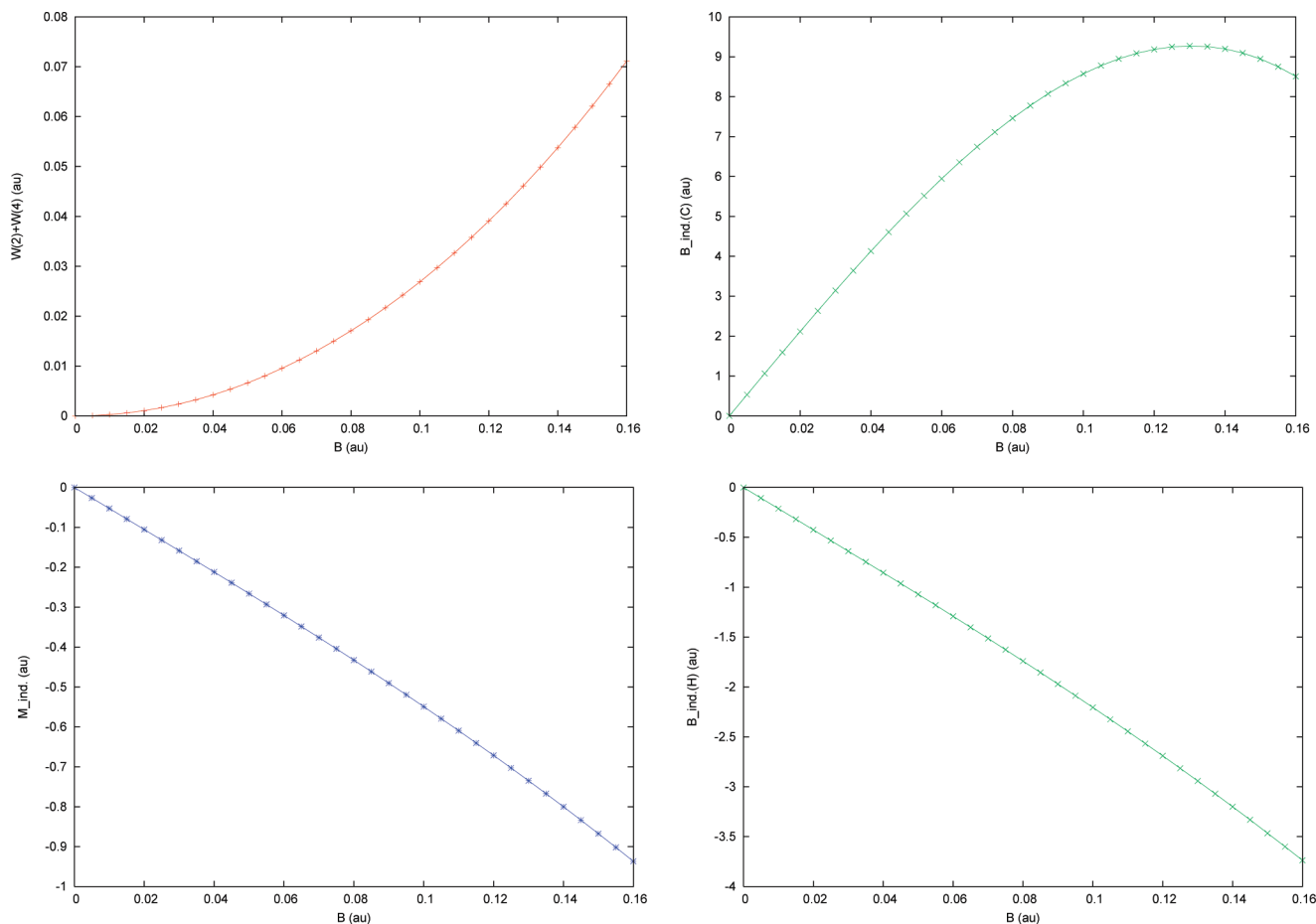


Figure 3. Response properties of the C_4H_4 molecule in a magnetic field normal to the molecular plane. Top left: Magnetic interaction energy. Top right: Magnetic field induced at the carbon nucleus. Bottom left: Induced magnetic moment. Bottom right: Magnetic field induced at the hydrogen nucleus.

Analogously, the values of B_{\perp}^{\ddagger} , in atomic units, corresponding to a change of sign of $\langle \hat{B}_{H\perp}^{\ddagger} \rangle$ in eq 7, are $\approx 5.9 \times 10^{-2}$ and $\approx 4.5 \times 10^{-2}$, for CH^+ and C_8H_8 at the CHF level, respectively. σ_{\perp}^H and Σ_{\perp}^H have the same sign in BH and C_4H_4 , compare for the monotonically decreasing green curves in Figures 1 and 3.

The values of B_{\perp}^{\ddagger} , in atomic units, for a sign inversion of the shielding of the heavier nucleus are $\approx 4.5 \times 10^{-2}$, $\approx 3.9 \times 10^{-2}$, and ≈ 0.13 , for BH, CH^+ , and C_4H_4 . The green curve for the shielding of the C nucleus in C_8H_8 decreases monotonically in Figure 4.

We observe that, within the assumption of cubic response, that is, neglecting higher nonlinear contributions, and within the CHF approximation, the critical B_m values of external magnetic field at which transition from induced orbital paramagnetism to diamagnetic behavior would occur in BH, ≈ 0.074 au, and CH^+ , ≈ 0.066 au, are much smaller than those predicted by Tellgren et al.,³⁰ 0.25 and 0.45 au, respectively. This seems to imply that perturbative approaches like those employed in the present investigations are basically unsuitable to describe a nonlinear response to extra-strong magnetic fields of diatomics such as BH and CH^+ , characterized by strong radial paramagnetism.

However, on increasing the size of the perturbed system, the discrepancies between the predictions in ref 30 and ours become smaller; compare the values for the clamped COT

molecule, ≈ 0.035 au, estimated by Tellgren et al. with $B_m \approx 0.027$ obtained here. This trend is expected, since the magnitude of the critical field $B_{\perp} = B_m$ decreases with the area of the system. In fact, orbital magnetism is proportional to the external magnetic flux; so that B_m varies approximately as the inverse of the area of the molecule.³⁰ Therefore, perturbative approaches like those applied here are accurate and can safely be used to rationalize a nonlinear response in systems spread over a large surface, which are most interesting for practical applications.^{43–46}

On the other hand, the radial component χ_{\perp} of the second-rank magnetizability of BH is known to be affected by electron correlation, as demonstrated by multiconfiguration self-consistent-field calculations.⁶⁹ Also, the KT3 results in Table 3 indicate that paramagnetism is lowered with respect to CHF. A similar reduction of χ_{\perp} for the CH^+ cation is observed in Table 6. Correlation contributions dramatically influence both hypermagnetizabilities and hypershieldings according to the present investigations. Tables 1–6 show that the $xxxx$, $xyyy$, $xxzz$, and $zxzx$ components of magnetic tensors are most affected.

Although the KT3 predictions obtained via the gaugeless basis sets depend strongly on the origin assumed in the calculation, much more than the corresponding CHF (which would be origin-independent for a complete basis set), inspection of the tables shows that electron correlation

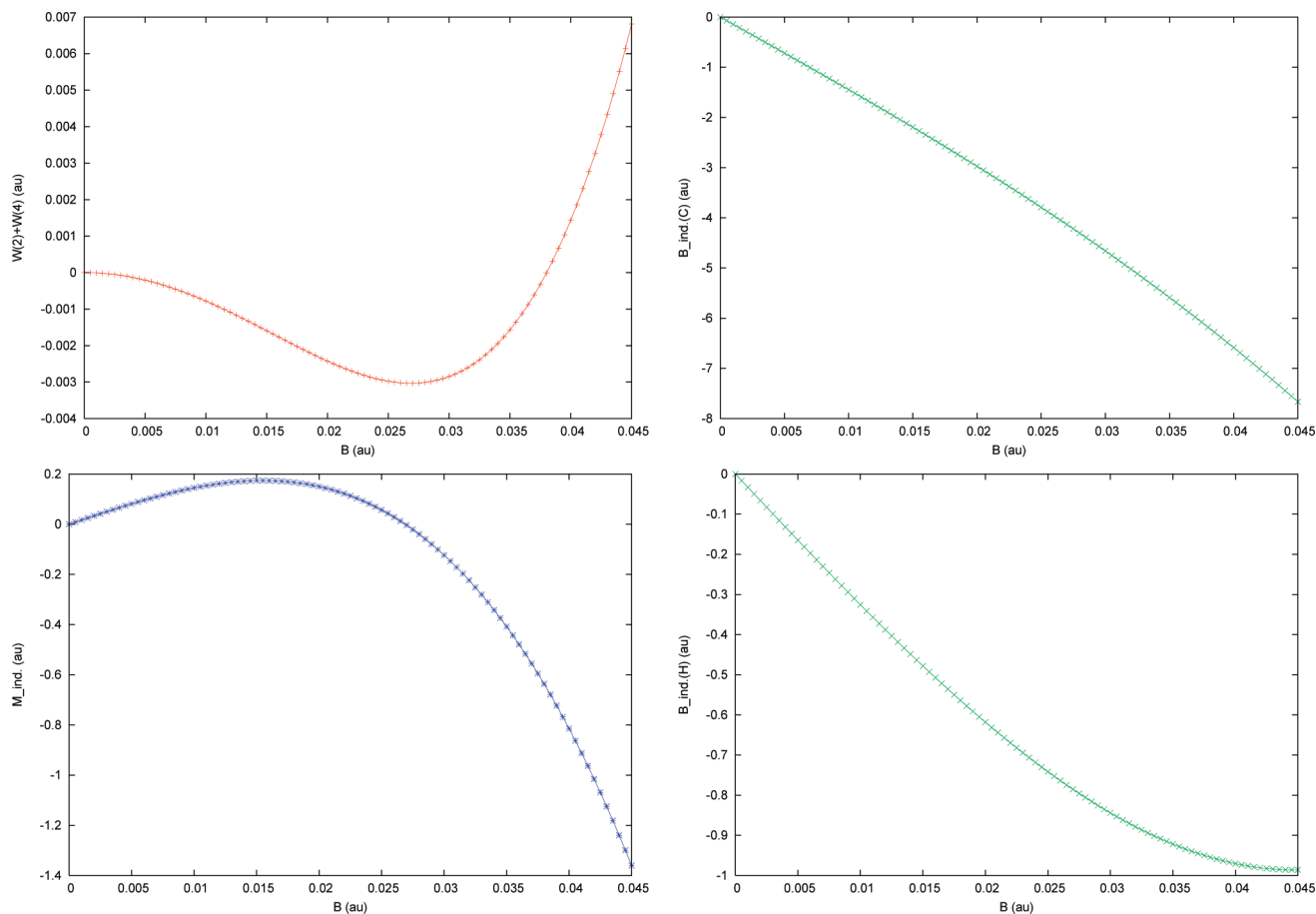


Figure 4. Response properties of the C_8H_8 molecule in a magnetic field normal to the molecular plane. Top left: Magnetic interaction energy. Top right: Magnetic field induced at the carbon nucleus. Bottom left: Induced magnetic moment. Bottom right: Magnetic field induced at the hydrogen nucleus.

provides a huge positive contribution to X_{\perp} of paramagnetic diatomics. The difference between CHF and DFT KT3 estimates is as big as $\approx 2 \times 10^3$ au for BH and $\approx 1 \times 10^4$ au for CH^+ , for the gauge origin on the center of mass. Quite remarkably, the correlation contributions to $X_{\perp} \equiv X_{zzzz}$ of cyclobutadiene and COT are negative. However, for the gauge origin on the center of mass, we calculated ≈ -43 au for the former, see Table 9, and $\approx -7 \times 10^5$ au for the latter, Table 12, at the KT3 level. Enormous changes were found also for Σ'_{\perp} , KT3 estimates being in many cases an order of magnitude smaller than those of CHF.

Notwithstanding the evident lack of accuracy of our common origin KT3 calculations of X_{\perp} and Σ_{\perp} , the results obtained here indicate that either perturbative or nonperturbative³⁰ calculations not taking electron correlation into account are limitedly reliable for predicting critical values of the applied magnetic field B_m at which the interaction energy changes sign in systems such as BH and CH^+ . One can therefore conclude that transition from orbital induced paramagnetism⁵⁶ to diamagnetism should occur at much smaller values of critical B_m than those predicted by CHF or RPA calculations not taking electron correlation into account.

Eventually, the magnitude of theoretical values obtained in this study and in a previous one for nitroso and diazene compounds⁵⁵ seem to indicate that nuclear magnetic hyper-shieldings can be better candidates than hypermagnetizabili-

ties for experimental detection of nonlinear magnetic response. Nuclear magnetic resonance spectroscopy would yield the best practical option.^{31,32}

IV. Concluding Remarks and Outlook

The present study provides reasonable answers to the basic questions (i–iv) raised in section II: (i) Perturbative CHF-RPA approaches to nonlinear response neglecting contributions higher than fourth order in the applied magnetic field may be insufficiently reliable for accurate estimates of interaction energy in closed-shell compounds of a small size such as BH and CH^+ , characterized by strong induced orbital paramagnetism in the singlet ground state. The interpretation of the highly nonlinear behavior, and the prediction of the magnetic field values $B_{\perp} = B_m$ and $B_{\perp} = B_m^*$, at which transition from paramagnetism to diamagnetism would occur in these systems, seems to require hypermagnetizability and hypershielding tensors higher than the fourth-order $X_{\alpha\beta\gamma\delta}$ and $\Sigma'_{\alpha\beta\gamma\delta}$ in eqs 1–4. However, the CHF perturbation method turns out to be useful for molecules as big as clamped C_8H_8 , for which satisfactory agreement with nonperturbative calculations^{29,30} was obtained. (ii) A nonlinear response can in principle be detected by measuring magnetic-field-dependent magnetizabilities and hypermagnetizabilities via a superconducting quantum interference device (SQUID). On the other hand, according to previous studies,⁵⁵ deviations

from a linear response would more easily be observed by measurements of magnetic hypershielding at the nuclei via NMR spectroscopy. The magnitude of calculated $\Sigma_{\alpha\beta\gamma\delta}^I$ is big in clamped C_8H_8 , suggesting that compounds containing this moiety may be potential candidates for detection. Cyclic species with bigger area are best suited for experimental observation of nonlinear contributions to a global molecular property such as the interaction energy $W_a - W_a^{(0)}$, eq 1, and for determination of the critical field B_m , as B_m decreases with system area. However, nonlinear response can in principle be observed also in small-sized species by investigating local effects on nuclear hypershielding. (iii) According to the present study, correlation plays a major role, and it dramatically affects the magnitude of calculated fourth-rank response tensors. Therefore, reliable predictions of hypermagnetizabilities and magnetic hypershielding at the nuclei would only be obtained by theoretical methods accounting for electron correlation. Furthermore, values of X_{\perp} predicted via KT3 in BH and in CH^+ are smaller than CHF's, which seems to imply that, at variance with (i), perturbative approaches limited to cubic response may be applicable at levels of theory taking electron correlation into account. In these diatomics, Σ_{\perp}^I calculated via DFT methods for boron and carbon are also smaller than CHF's. (iv) Therefore, allowing for the previous points, the answer to the question posed in the title is likely to be in the affirmative: induced orbital paramagnetism of some closed-shell species selected ad hoc can be controlled, and transition from paramagnetic to diamagnetic behavior can probably be observed in a terrestrial laboratory.

Eventually, highly excited hydrogen atoms and Rydberg molecules in strong magnetic fields are a paradigm of a real system, showing the signature of quantum chaos.^{84–86} These species become chaotic as soon as the interaction of the electron with the magnetic field is of the same order of magnitude as the Coulomb interaction with the nucleus. The classical trajectories of the atomic electron undergo a transition from regularity to chaos as the field strength increases. Therefore, the interplay of regularity and chaos for highly excited Rydberg atoms and molecules in strong magnetic fields would possibly make difficult, or even preclude, in the majority of cases, experimental determination of hypermagnetizabilities and nuclear hypershieldings of rank higher than the fourth, and rationalization of nonlinear effects beyond the cubic in the field strength, either via perturbation theory or nonperturbative techniques, may become problematic.

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