

Magnetic-field-dependent molecular susceptibility

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The magnetic susceptibility to second order in the magnetic field is calculated for the molecules H_2 , HF, and BH. The finite perturbation method and basis sets of gauge-invariant Gaussian functions are used.

The possibility that the magnetic field dependence of the nuclear magnetic shielding for some substances could be observed in high-precision experiments in strong magnetic fields has been pointed out by Ramsey.¹ By considering a typical term in the fourth-order perturbation calculation of the energy, he estimated the general magnitude of the field-dependent term in nuclear magnetic shielding. Since the nuclear magnetic shielding and the molecular magnetic susceptibility are two different measurable representations of the same induced electronic currents, one expects a similar field dependence of the molecular susceptibility. In our earlier calculations² we have shown that the finite perturbation method is suitable for the calculation of the zero-order susceptibility. One of the advantages of the finite perturbation approach for the calculations of physical properties of molecules is that it can be easily extended to higher-order properties.³ In this note we show that it is possible to calculate a reliable field-dependent term of the susceptibility by the finite perturbation method.

The total molecular susceptibility χ^T is the sum of the usual field-independent susceptibility $\chi^{(0)}$ and terms proportional to the magnetic field:

$$\chi^T = \chi^{(0)} + \chi^{(2)} B_0^2 + \dots,$$

where $\chi^{(2)}$ is the coefficient of the second-order susceptibility. The odd powers of B_0 in the above equation vanish because the magnitude of the susceptibility must be independent of the direction of the magnetic field. The susceptibility components can be deduced from the molecular energies cal-

culated for different orientations and magnitudes of the magnetic field.

In our calculations the energies were calculated with the single-determinant molecular wave functions in the presence and in the absence of the external magnetic fields by use of Roothaan-Hartree-Fock equations. To avoid the gauge dependence of the energy, we used gauge-invariant Gaussian basis functions.

The basis set used for the hydrogen molecule is double-zeta⁴ completed with a single set of polarization functions (p_x, p_y, p_z) with the exponents equal to 1. At fixed internuclear distance $R = 1.400$ a.u. it gives the value -1.131197 for the molecular energy in the absence of the magnetic field. The energies at two different magnetic field densities of the order of 10^8 T were calculated for each principal direction to evaluate the zero-order and the second-order magnetic susceptibilities. The susceptibilities of HF ($R = 1.733$ a.u.) and BH ($R = 2.329$ a.u.) were calculated with the basis combined from the $4s2p$ set for the heavier nucleus⁵ and the $1s$ contraction of four primitive functions⁶ for H. In addition, for a rough estimation of the basis-set dependence of the second-order susceptibility, one calculation on HF (denoted by II in Table I) was done with the smaller basis^{5,6} combined from the $2s2p$ set for F and a $1s$ contraction of two primitive functions for H.

Results are given in Table I. Comparison of the susceptibility components of H_2 with those calculated by other authors shows that the basis set used predicts the zero-order susceptibility within the error of a few percent.⁷ The basis sets used

TABLE I. Zero-order and second-order magnetic susceptibilities. The units are 10^{-6} erg G⁻² mol⁻¹ for $\chi^{(0)}$, 10^{-25} erg G⁻⁴ mol⁻¹ for $\chi^{(2)}$, and 10^{-10} for $-\chi^{(2)} B_0^2 / \chi^{(0)}$. $B_0 = 6.26$ T (see Ref. 1).

Molecule	$\chi_L^{(0)}$	$\chi_L^{(2)}$	$-\chi_L^{(2)} B_0^2 / \chi_L^{(0)}$	$\chi_{II}^{(0)}$	$\chi_{II}^{(2)}$	$-\chi_{II}^{(2)} B_0^2 / \chi_{II}^{(0)}$
H_2	-4.078	1.80	1.7	-3.508	1.18	1.3
HF	-9.07	2.88	1.2	-8.48	0.16	0.07
HF(II)	-10.51	2.84	1.1			
BH	36.76	-5040	540	-10.70	1.07	0.39

for the calculations of HF and BH are much more limited, and the estimated error for the zero-order susceptibility is about 20%. The rough test of the susceptibility basis-set dependence shows that this dependence of the second-order term is much smaller than of the zero-order one. The ratios $-\chi^{(2)}B_0^2/\chi^{(0)}$ are calculated at a magnetic flux density $B_0 = 6.26$ T. They agree quite well

with the analogous ratio for the nuclear magnetic shielding estimated by Ramsey¹ to be 7×10^{-10} . The most outstanding result is that for $\chi_1^{(2)}$ of BH which must be related to the zero-order paramagnetism of this molecule. It is worth noting that for all three molecules the second-order term diminishes the diamagnetism or paramagnetism of the zero-order term.

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⁷Proton magnetic shielding components in hydrogen molecule calculated with the same basis set are $\delta_{\perp} = 26.09$ ppm and $\delta_{\parallel} = 27.84$ ppm.