The Magnetic Properties of the Hydrogen Molecule

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For diamagnetic molecules it has been shown[1] that the so-called high frequency or paramagnetic contributions to the induced current density produced by an external magnetic field — whence: to the nuclear shielding and the susceptibility tensors $\hat{\sigma}$ and $\hat{\chi}$ — can be treated by means of scalar velocity potentials. Only those parts of the currents need to be considered, which are proportional to the field.

Let n represent a quantum mechanical one-particle density when the field is absent (or a semiclassical, i.e. a Thomas-Fermi density, or even a classical charge distribution), then the electric current resulting from applying a static field $\boldsymbol{B}$ may be written as:

$$\boldsymbol{j} = e\,n(\gamma \boldsymbol{A} + \nabla f_{\boldsymbol{A}}), \quad \gamma = e/m, \qquad (1)$$

where e and m are charge and mass of the particle (the electron), $\boldsymbol{A}$ is an arbitrary choice of the vectorpotential used to describe the field. Practical units are used throughout.

$f_{\boldsymbol{A}}$ is a velocity potential for the paramagnetic part of the current or may be thought of as being a gauge transformation adapted to the geometry of n; this quantity is a functional of $\boldsymbol{A}$ and can be determined from:

$$\operatorname{div} \boldsymbol{j} = n \cdot \Delta f_{\boldsymbol{A}} + \nabla n(\gamma \boldsymbol{A} + \nabla f_{\boldsymbol{A}}) = 0 \qquad (2)$$

with boundary conditions discussed in [1]. Molecular N-particle densities can be handled similarly by superposition of orbital contributions. To Eq. (2) there corresponds a variation principle:

$$\delta_f \int \mathrm{d}\tau\, n \nabla f(\nabla f + 2\gamma \boldsymbol{A}) = 0\,, \qquad (3)$$

which proves to be most efficient for an approximate determination of f, if one is not willing to use numerical techniques for the solution of the partial differential equation (2).

Some of the basic arguments of this method pertaining to the one electron case have been used in an approximate[2] calculation of the moment of inertia of H_2. According to the usual definitions, the $\hat{\sigma}$- and $\hat{\chi}$-tensors are obtained from Eq. (1) by classical electrodynamics[3]; in the following, directly the scalar mean quantities are considered.

For the description of the unperturbed ground state of the hydrogen molecule Coulson's LCAO-MO function (shielded)[4] as well as SCF functions with different screening parameters[5] α have been chosen. For these densities, the use of the outlined method contains no approximation.

Cartesian coordinates (x, y, z) are introduced, the field pointing parallel to the z-axis, the protons being located at $\pm R$ on the y-axis respectively, as well as prolate spheroidal coordinates (μ, ν, φ) defined by:

$$\mu = \frac{1}{2R}(r_1 + r_2)\,, \quad \nu = \frac{1}{2R}(r_1 - r_2)\,,$$
$$\cos\varphi = x/\sqrt{x^2 + z^2}\,,$$

where r_i design the distances to the protons. Choosing $\boldsymbol{A}$ as:

$$\boldsymbol{A} = 1/2\, \boldsymbol{B} \times (\boldsymbol{r} - \boldsymbol{R}_0) \qquad (4)$$

application of the variation principle in order to determine $\boldsymbol{R}_0$ leads to $\boldsymbol{R}_0 = 0$. It has been known for some time[6] that taking $\boldsymbol{R}_0$, the origin of the vectorpotential, to be the center of electronic charge causes χ^{d} to be at a minimum. Due to the small excentricity of H_2, all paramagnetic parts are reduced to a few percent of the total valus, conforming however to current notation, we refer the results to the nuclei.

It follows from (2) that f is proportional to $\cos\varphi$, it is convenient to expand as

$$f = \frac{R\gamma}{2}\, x\, \Theta \sum_{p,q} c_{pq}\, \mu^p \nu^q\,, \qquad (5)$$

where the range of q is restricted to odd positive integers by symmetry. From a model calculation

$$\left[n \sim \mu^{-6} \text{ corresponding to } f = \frac{R\gamma}{2}\, \frac{xy}{\mu(\mu+1)} \right]$$

it appears essential to include negative powers of μ. Θ symbolizes a cut-off factor at infinity in order to obey boundary conditions[1]; due to the exponential decay of n it may be set equal to unity, the expansion coefficients $\{c\}$ are computed from (3).

The results together with some reference values [7–16] are collected in Table 1; they compare favorably with existing calculations by different methods [10, 11, 14, 15, 17]. As many as 35 terms in the trial functions have been considered simultaneously, scattered in different fashions as $-10 \leq p \leq 10$, $1 \leq q \leq 13$. High powers of ν are quite unimportant, it is vital however to allow for a μ-dependence. Negative and positive q-values are about equally effective. If it is possible to represent f over the range of the molecular charge distribution by (5), our results should be as accurate as the description of the unperturbed groundstate. The diamagnetic contributions are reasonably given by the

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Groundstate described by:	Self-consistent field functions (Ref. [5]) $\alpha = 0.75$	$\alpha = 0.85$	$\alpha = 0.9$	$\alpha = 0.95$	$\alpha = 1.0$	LCAO-MO (Ref. [4])	Reference values
σ^d [ppm] (Origin at H)	32.213	32.226	32.228	32.234	32.245	32.362[a, b, c]	32.1 ± 0.1 Ref.[16] 32.012 Ref.[18]
σ^p [ppm] (Origin at H)	– 5.694	– 5.730	– 5.743	– 5.755	– 5.768	– 5.040[a] – 4.903[b] – 5.018[c]	-5.9 ± 0.3 Ref.[10] -5.6 ± 0.1 Ref.[12]
σ [ppm]	26.520	26.495	26.485	26.479	26.477	27.322[a] 27.459[b] 27.343[c]	26.2 ± 0.4 Ref.[10] $26.5_5 \pm 0.3$ Ref. [9]
C_α [kc/sec]	116.80	116.19	115.98	115.77	115.56	124.7[a]	113.9 ± 0.1 Ref.[13] (exp.)
χ^d [m³/mole] $\cdot 10^{10}$	– 0.5147	– 0.5146	– 0.5139	– 0.5125	– 0.5103	– 0.5037[a, b, c]	– 0.5061 Ref. [5] – 0.5201 Ref. [18]
χ^p [m³/mole] $\cdot 10^{10}$	0.00848	0.00846	0.00845	0.00844	0.00841	0.0141[a] 0.0177[b] 0.0140[c]	0.01063 Ref.[7,12]
χ [m³/mole] $\cdot 10^{10}$	– 0.5062	– 0.5061	– 0.5055	– 0.5041	– 0.5019	– 0.4895[a] – 0.4859[b] – 0.4897[c]	– 0.501 ··· – 0.495 (Ref.[8], exp.)

[a] This paper, [b] GIAO method, [c] GIAO with variation.

Table 1. The average magnetic properties of H_2.

wavefunctions used, as well as the shielding and correspondingly the spin rotational constant C_α by the SCF functions, the LCAO description being less satisfactory. The paramagnetic part of χ is not very well represented — corresponding to the weighting in the surface of the molecule — previous calculations [7,11] of that quantity (and the rotational magnetic moment) scatter by a factor 10. Experimentally, χ^p amounts to 2.1% of the total susceptibility, whereas our calculations give only 1.7%.

The accuracy of the computations is to five significant digits. However, rather large error bars should be admitted on the shielding values: our σ^d differ from the best value [18], no averaging on vibronic states is included and the calculations are carried out at the theoretical equilibrium distance. MUSHER [9] claims that these neglects will amount to about 0.4 ppm. For similar reasons one should not take the total susceptibility values too literally within the limits of a few percent.

We add a remark on the method of "Gauge Invariant Atomic Orbitals" (GIAO) [10,14]. In conjunction with the shielded Coulson wavefunction this procedure gives a result for the imaginary part of the wavefunction which is equivalent[1] to:

$$f_{\mathrm{GIAO}} = -\frac{R\gamma}{2}\, x \,\mathrm{tgh}(R c \nu), \quad c = 1.197/a_0, \tag{6}$$

a_0 being the radius of the first Bohr orbit. Writing the exact solution as $f = f_{\mathrm{GIAO}}\, g(\mu, \nu)$, Eq. (2) reads:

$$\Big\{(\mu^2-1)\frac{\partial^2}{\partial\mu^2} + [4\mu - 2\beta(\mu^2-1)]\frac{\partial}{\partial\mu} + (1-\nu^2)\frac{\partial^2}{\partial\nu^2} + [2\beta(1-\nu^2)\coth\beta\nu - 4\nu]\frac{\partial}{\nu\partial} - 2\beta[\mu + \underline{2\nu + \nu\,\mathrm{tgh}\,\beta\nu}]\Big\}\, g = -2\beta[\mu + \underline{\nu\coth\beta\nu}], \tag{2b}$$

$$\text{where } \beta = c \cdot R.$$

If the terms we have underlined could be neglected, the solution would be $g = 1$. The approximate solution f_{GIAO} is in error mainly in the neighbourhood of the protons; it is this region however, which is most important for the determination of the nuclear shielding. Taking g to be a constant, application of Eq. (3) leads to $g = 0.79$. In the table the results with that modified function (6) are quoted as "GIAO with variation". As compared with variational solutions, the GIAO method seems to introduce quite visible errors.

In the figure a vector map of the induced current density distribution is represented, which is calculated from the SCF function that gives the minimum of the total energy ($\alpha = 0.95$) with the most successful trialfunction for (3). None of the other wavefunctions or variational solutions show marked differences in comparison with this diagram, which is to be contrasted with a plot given in the literature (Fig. 3 of Ref. [10]).

In conclusion, the method employed here appears to produce reliable results in this simple case; the remaining errors are due to the errors in the wavefunctions of the unperturbed molecule. In particular, the values for the average shielding are probably better than the results for the susceptibility; this might be attributed to the appearance of $1/r_i$ terms in the Hamiltonian for the electronic motion and the neglect of correlation in the considered approximations of the wavefunction.

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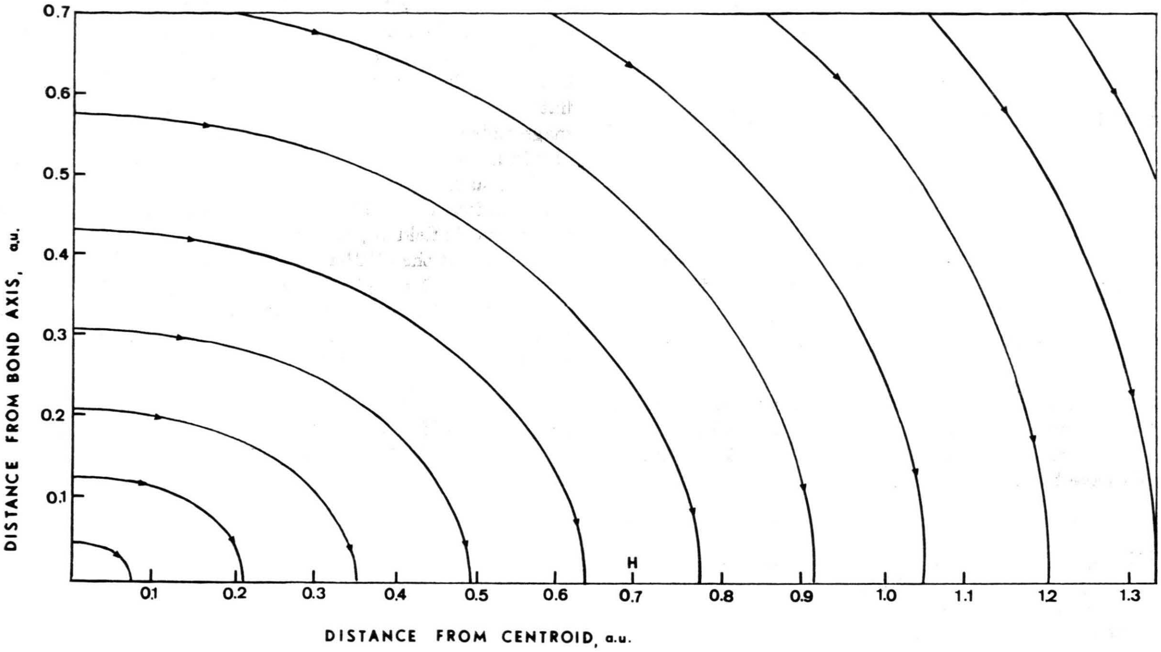

Fig. 1. Vector direction map of electric current density in H_2 the field is directed out of the plane of the paper.