The Magnetic Properties of the Hydrogen Molecule

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For diamagnetic molecules it has been shown1 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 $\sigma$ and $\chi$ — 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 $B$ may be written as:

$$f = e n (\gamma A + \nabla f_A), \quad \gamma = e/m,$$

where $e$ and $m$ are charge and mass of the particle (the electron), $A$ is an arbitrary choice of the vectorpotentual used to describe the field. Practical units are used throughout. $f_A$ 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 $A$ and can be determined from:

$$\text{div} f = \nabla \cdot f_A + \nabla (\gamma A + \nabla f_A) = 0$$

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 approximate2 calculation of the moment of inertia of $H_2$. According to the usual definitions, the $\sigma$- and $\chi$-tensors are obtained from Eq. (1) by classical electrodynamics; 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

$$(\text{shielded})^3$$ as well as SCF functions with different screening parameters $x$ 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 $(\mu, \nu, \varphi)$ defined by:

$$\mu = 1 + 2 R (r_1 + r_2), \quad \nu = 1 + 2 R (r_1 - r_2),$$

where $r_i$ design the distances to the protons. Choosing $A$ as:

$$A = \frac{1}{2} B \times (r - R_0)$$

application of the variation principle in order to determine $R_0$ leads to $R_0 = 0$. It has been known for some time3 that taking $R_0$, the origin of the vectorpotential, to be the center of electronic charge causes $d^2$ to be at a minimum. Due to the small eccentricity of $H_2$, all paramagnetic parts are reduced to a few percent of the total value, conforming however to current notation, we refer the results to the nuclei.

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

$$f = \frac{R \gamma}{2} x \cos \varphi \mu \varphi,$$

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

$$n \sim \mu^{-6} \text{corresponding to} f = \frac{R \gamma}{2} x \cos \varphi \mu (\mu + 1),$$

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

The results together with some reference values7–16 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 $-10 \leq \mu \leq 10, 1 \leq q \leq 13$. High powers of $\varphi$ are quite unimportant, it is vital however to allow for a $\mu$-dependence. Negative and positive $\varphi$-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 magnetic contributions are reasonably given by the

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2 J. ESPER, Phys. Rev. 102, 1254 [1956].
5 C. C. J. ROOTHEAM and W. KOLOS, Rev. Mod. Phys. 32, 265 [1960].
10 D. E. O'REILLY, Progr. XMR Spectrosc., 2, 1 [1967].
Groundstate described by: $x = 0.75$  
Self-consistent field functions (Ref. 5)  
$a = 0.75 \quad a = 0.85 \quad a = 0.9 \quad a = 0.95 \quad a = 1.0$  
LCAO-MO (Ref. 4)  
Reference values

<table>
<thead>
<tr>
<th>$\sigma^d$ [ppm] (Origin at H)</th>
<th>$\sigma^p$ [ppm] (Origin at H)</th>
<th>$\sigma$ [ppm]</th>
<th>$C_z$ [kcal/sec]</th>
<th>$\chi^d$ [m$^3$/mole $\cdot 10^{10}$]</th>
<th>$\chi^p$ [m$^3$/mole $\cdot 10^{10}$]</th>
<th>$\chi$ [m$^3$/mole $\cdot 10^{10}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.213</td>
<td>-5.694</td>
<td>26.520</td>
<td>116.80</td>
<td>-0.5147</td>
<td>0.00848</td>
<td>-0.5062</td>
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<tr>
<td>32.226</td>
<td>-5.730</td>
<td>26.495</td>
<td>116.19</td>
<td>-0.5146</td>
<td>0.00846</td>
<td>-0.5061</td>
</tr>
<tr>
<td>32.228</td>
<td>-5.743</td>
<td>26.485</td>
<td>115.98</td>
<td>-0.5139</td>
<td>0.00845</td>
<td>-0.5055</td>
</tr>
<tr>
<td>32.234</td>
<td>-5.755</td>
<td>26.479</td>
<td>115.77</td>
<td>-0.5125</td>
<td>0.00844</td>
<td>-0.5041</td>
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<tr>
<td>32.245</td>
<td>-5.768</td>
<td>26.477</td>
<td>115.56</td>
<td>-0.5103</td>
<td>0.00841</td>
<td>-0.5019</td>
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<tr>
<td>$32.362^{a,b,c}$</td>
<td>-5.040</td>
<td>27.322</td>
<td>124.7a</td>
<td>-0.5207</td>
<td>0.0141</td>
<td>-0.5085</td>
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<td>-4.903</td>
<td>27.433</td>
<td>113.9 ± 0.1</td>
<td>-0.5061</td>
<td>0.0140</td>
<td>-0.4895</td>
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<tr>
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<td>-5.018</td>
<td>27.343</td>
<td>26.2 ± 0.4</td>
<td>-0.5055</td>
<td>0.0140</td>
<td>-0.4897</td>
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<td>-0.4897</td>
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<td>(Ref. 8, exp.)</td>
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</tbody>
</table>

$\sigma^d$  and $\sigma^p$ differ from the best value $a = 1.197/\alpha_0$, $\alpha_0$ being the radius of the first Bohr orbit. Writing the exact solution as $f = f_{\text{GIAO}}(\mu, v)$, Eq. (2) reads:

\[
\begin{align*}
(\mu^2 - 1) \frac{\partial^2}{\partial \mu^2} + [4\mu - 2\beta(\mu^2 - 1)] \frac{\partial}{\partial \mu} + (1 - v^2) \frac{\partial^2}{\partial v^2} \nonumber \\
+ [2\beta(1 - v^2) \coth \beta v - 4v] \frac{\partial}{\partial v} \\
- 2\beta[\mu + 2v + v \tanh \beta v] \frac{\partial}{\partial \mu} \nonumber \\
\end{align*}
\]

with $\beta = \frac{c}{\alpha} R$.  

If the terms we have underlined could be neglected, the solution would be $g = 1$. The approximate solution $f_{\text{GIAO}}$ 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 ($x = 0.95$) with the most successful trial function for (3). None of the other wave functions 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 $1/\alpha_0$ terms in the Hamiltonian for the electronic motion and the neglect of correlation in the considered approximations of the wavefunction.

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*$a$ This paper, $b$ GIAO method, $c$ GIAO with variation.
Fig. 1. Vector direction map of electric current density in $\text{H}_2$ the field is directed out of the plane of the paper.