Variational Calculation of Magnetic Shielding of Protons in the Hydrogen Molecule*

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When an atom or molecule is placed in an external magnetic field, the electron distribution becomes distorted and the system acquires a field-dependent magnetic moment. Two independent observable effects result. The magnetic moment of the system interacts with the external field (diamagnetism) or with the field of the nuclei (chemical shift) giving rise to terms of order $\mu_{\mathrm{el}}H^2$ and $\mu_{\mathrm{nuc}}H$ in the electronic energy. Computation of the paramagnetic parts of either the diamagnetic susceptibility or the magnetic shielding requires a knowledge of the wave function of the system to first order in the external magnetic field. Conventional perturbation theory results in infinite series[1,2] which cannot be reliably summed. For this reason we have sought a variational function which happily has been discovered by Tillieu and Guy.[3] They used for the electronic wave function of the hydrogen molecule the form

$$\psi=\psi_0(1+\mathbf{g}\cdot\mathbf{H}), \tag{1}$$

where ψ_0 is the unperturbed wave function. With the magnetic field in the y direction perpendicular to the axis of the molecule, g_y is taken as

$$g_y=iax_cz_c, \tag{2}$$

the suffix c indicating that distances are measured from the center of the molecule. In order to obtain a, the expectation value of the energy of the electrons to terms in H^2 is now minimized.[4] Proper attention must be paid to the gauge transformations involved in changing the origin from the center of the molecule to a proton. It may then be shown, by using (1) and (2), that the coefficient of terms $\mu_{\mathrm{nuc}}H_y$ in the energy is

$$\sigma_{yy}=\alpha^2\left\{\left\langle\frac{1}{r}\right\rangle\frac{\langle x_c^2\rangle-\langle z_c^2\rangle}{\langle x_c^2\rangle+\langle z_c^2\rangle}\left\langle\frac{z^2-x^2}{r^3}\right\rangle -\frac{R}{2}\left\langle\frac{z}{r^3}\right\rangle\left[1+\frac{\langle x_c^2\rangle-\langle z_c^2\rangle}{\langle x_c^2\rangle+\langle z_c^2\rangle}\right]\right\},$$

where α is the fine structure constant and R the proton-proton distance. The expectation values are taken over the ground state; the unsuffixed variables refer to distances measured from a proton. Because the hydrogen molecule is axially symmetric, the effective shielding constant observed in a rotating molecule is given by $\sigma=\frac{2}{3}\sigma_{yy}$. Using Coulson,[5] Wang,[6] and Weinbaum[7] functions for the hydrogen molecule, we have obtained for the "second-order" paramagnetic term the values $\sigma_p=(-0.53, -0.49, -0.52)\times10^{-5}$, respectively. These values compare very favorably with that of Ramsey[2] who obtained it ingeniously from the observed value of the rotational magnetic field in the H_2 molecule, *viz.*,

$$\sigma_p=-0.56\times10^{-5}. \tag{6}$$

The first term σ_d, *viz.*, the diamagnetic shielding constant, has been obtained by Anderson[2] as 3.24×10^{-5} from Nordsieck's wave function, so that the values for the total σ obtained by us are very close to Ramsey's value

$$\sigma=2.68\times10^{-5}. \tag{7}$$

The advantage of our method is that one does not need a knowledge of the wave functions or energies of the excited states of the molecule. A variational method was earlier proposed by Hornig and Hirschfelder.[8] It has the disadvantage that it leads to divergences when applied to the s and p atomic states, which are the important ones for the lighter molecules.

Details of the method as well as a table of values of σ for a number of wave functions for the hydrogen molecule will be published later. The authors are grateful to Professor J. O. Hirschfelder for helpful communication and to the staff of the Cornell Computing Center for assistance in numerical work.

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Ferroelectricity of Glycine Sulfate

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We have discovered that glycine sulfate, $(CH_2NH_2\text{-}COOH)_3H_2SO_4$,[1] and its isomorphous selenate are ferroelectric. The Curie point of the sulfate is 47°C and that of the selenate is 22°C. As in all ferroelectrics which are not cubic above their Curie points, there is only one ferroelectric axis. For glycine sulfate at room temperature the spontaneous polarization is 2.2×10^{-6} coul/cm² and the coercive field is 220 v/cm.

It is tempting to regard this result as confirmation of a general mechanism operative in such ferroelectric materials as ammonium sulfate,[2] and with it the same for the guanidine aluminum sulfate and its isomorphs (GASH)[3] and some of the alums.[4]

In the infrared absorption of ammonium sulfate[5] there are two characteristic features below its Curie point. The 3.3μ band due to the NH_4^+ shows a change similar to that in the transition region of ammonium chloride. At the same time, the absorption spectrum due to the SO_4 tetrahedra shows a similar rearrangement. One could therefore assume that an ordinary ammonium transition acts as a trigger to induce a moment in the SO_4^{--} groups. The mechanism would be thus strongly reminiscent of the one causing ferroelectricity in KH_2PO_4 as described by Slater.[6] This point of view suggests a formal similarity among the ferroelectric sulfates thus far encountered regardless of crystal structure or water of crystallization. The role of ammonium is played by guanidinium in GASH, by methylamine or urea in some alums, and by glycine in the material here reported.

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Nuclear Resonance Saturation Effects and Multiple-Quantum Transitions

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The theory presented by Bloch[1] indicates that different lines of a spectrum observed by using high-resolution nuclear magnetic resonance techniques may have different relaxation times. Differences in line widths within a spectrum have been observed[2–4]; however, in many cases magnetic field inhomogeneities prevent quantitative measurements. Saturation techniques may be employed to demonstrate differences in relaxation times even though magnetic field inhomogeneities may obscure the natural widths.

A simple case treated by Bloch[1] is a nuclear spin system consisting of two identical nuclei with spin $\frac{1}{2}$ and Larmor frequencies which differ because of a chemical shift. The molecule 2-bromo-5-chlorothiophene is of this type and its spectrum under conditions of low radio-frequency fields has been previously investigated.[3] Interesting modifications of this spectrum have been observed with radio-frequency fields of large amplitudes by using a Varian Model 4300 Spectrometer with a 30-Mc radio-frequency unit.

Spectra obtained at three different levels of radio-frequency power are shown in Fig. 1. Spectrum (a) was made with a radio-frequency field low enough to avoid saturation of any of the lines. In spectrum (b) the radio-frequency field has been increased by a factor of approximately 3.4 while the gain of the receiver has been decreased by the same factor. The size of the outside pair of lines is nearly the same in both spectra, indicating that they are not saturated, while the height of the central pair of lines has decreased by approximately 35%. Spectrum (c) was obtained upon increasing the radio-frequency field by another factor of approximately 3.4 with a corresponding decrease in receiver gain. Here the outside pair of lines have also been partially saturated.

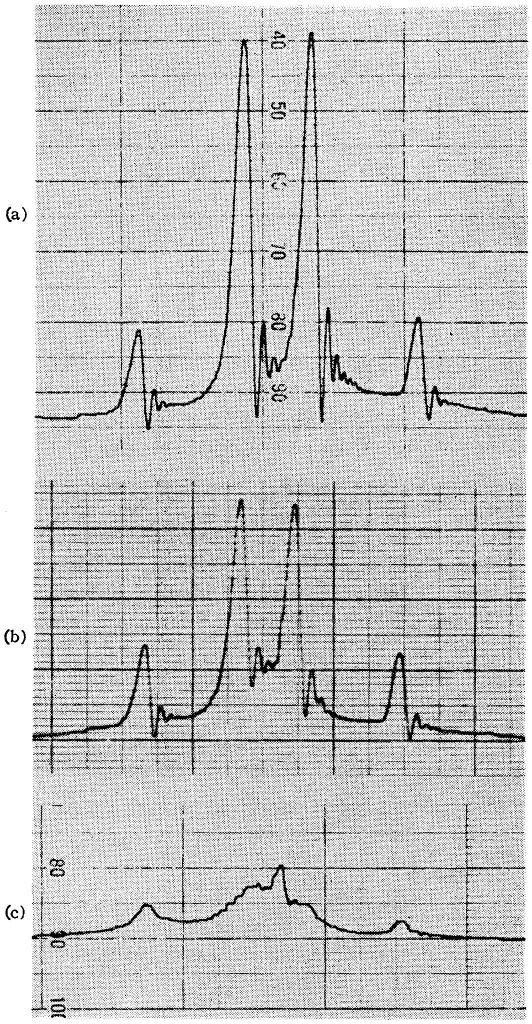

Fig. 1. Nuclear magnetic resonance spectra of 2-bromo-5-chlorothiophene. (a) Spectrum taken using low radio-frequency power. (b) Radio-frequency field increased by approximately 3.4 with a corresponding decrease in radio-frequency amplifier gain. (c) Radio-frequency field increased by another factor of 3.4 with a corresponding decrease in radio-frequency amplifier gain. The spacing between the two extreme peaks is approximately 10 cps at 30 Mc/sec and the sweep rate is approximately 5 cps/min.

Bloch[1] has shown that for well-resolved lines the nuclear resonance signal for a transition between levels