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, $(CH_2NH_2COOH)_3H_2SO_4$,[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]