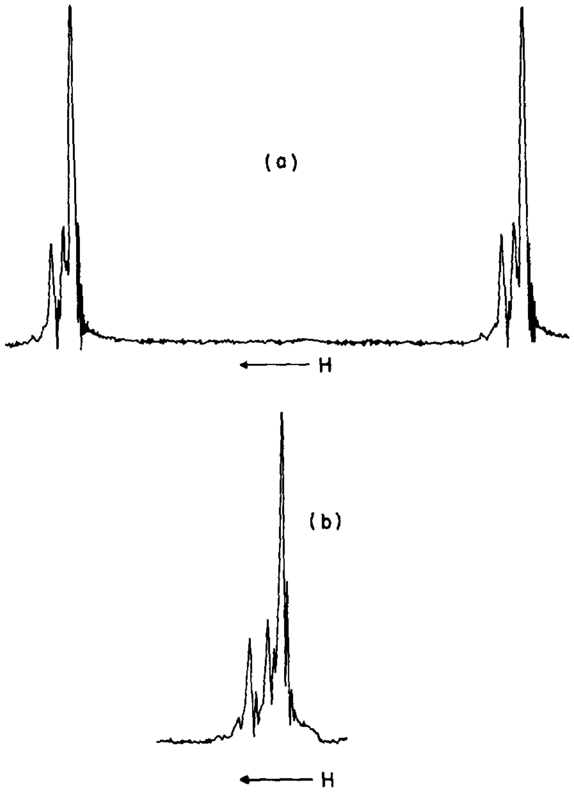

FIG. 1. (a) The proton magnetic resonance of a mixture of $^{15}NH_3$, $^{15}NH_2D$, and $^{15}NHD_2$. (b) Details of one of the two groups of lines in (a).

urement. This result has been used repeatedly in determining proton–proton spin couplings from measured proton–deuteron coupling constants. When multiplied by γ_H/γ_D a value of 10.35±0.80 cps is obtained for the proton–proton coupling constant. It is also likely that this value is independent of the fact that ^{15}N-ammonia was used instead of ^{14}N-ammonia.

As a preliminary step to the theoretical investigation of the proton spin–spin coupling in ammonia we have evaluated the contact part of the spin–spin interaction using the molecular orbital perturbation treatment[2] and the SCF MO wavefunctions of Duncan[3] and Kaplan.[4,5] We obtain a value of $87.2/\Delta E$ cps with the Duncan function and $52.2/\Delta E$ cps with the Kaplan function, where ΔE is a mean excitation energy in electron volts and probably lies between 7 and 9 eV. The only difference between the two wavefunctions is that the Duncan function uses Slater orbitals for nitrogen while Kaplan uses the nitrogen functions of Hartree. In both cases a numerically positive result is obtained. Any further discussion of these results should be deferred until the sign of the coupling has been determined.

TABLE I. Spin coupling constant J and isotopic chemical shifts δ obtained from the 40-Mc/sec proton magnetic resonance of $^{15}NH_3$, $^{15}NH_2D$, and $^{15}NHD_2$.

	J_{HN}(cps)	J_{HD}(cps)	δ(ppm)
$^{15}NH_3$	61.2±0.9		0
$^{15}NH_2D$		1.54±0.12	0.029±0.002
$^{15}NHD_2$		1.54±0.12	0.053±0.003

The second interesting feature of the experimental results is the almost linear variation of the isotope shift with successive deuterium substitution.

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Diamagnetic Nuclear Shielding Constants for Neutral Atoms*

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RECENTLY, Rustgi and Tiwari[1] have published the results of Hartree–Fock (HF) calculations of the nuclear dimagnetic shielding constants of several of the lighter elements. The purpose of this note is to present the results for the diamagnetic shielding constants for the neutral atoms from $Z=2$ to $Z=100$ using a Hartree–Fock electron density function for the atoms $Z=2$ to $Z=36$,[2] and a Thomas–Fermi–Dirac (TFD) electron density function for the atoms from 2 to 100. The diamagnetic shielding constant for the HF field can be written as

$$\sigma_D=\frac{1}{3}\alpha^2a_0\left\langle\frac{1}{r}\right\rangle=\frac{1}{3}Z\alpha^2a_0\left\{\sum_{i=1}^{2}{}^a\gamma_i\,{}^a\lambda_i-\sum_{j=1}^{M\leq 3}{}^b\gamma_j\right\},\qquad(1)$$

where the γ's and λ's are given in Ref. 2. For the TFD field σ_d can be written as

$$\sigma_d=\frac{1}{3}Z\alpha^2a_0\sum_{i=1}^{3}\gamma_i\lambda_i,\qquad(2)$$

where the constants are given in Ref. 3.

The results are presented in Table I. In the first column the TFD values are given while in the second and third columns the HF values from Eq. (1) and Ref. 1 are presented. The agreement between our values and those of Rustgi and Tiwari are quite good and attest to the accuracy of the analytical expressions presented in Ref. 2.

Table I. Diamagnetic nuclear shielding constants for the neutral atoms.

Z	TFD $\sigma_D\times10^5$ (Ref. 3)	HF $\sigma_D\times10^5$ (Ref. 2)	HF $\sigma_D\times10^5$ (Ref. 1)	Z	$\sigma_D\times10^5$ TFD
2	8.937	5.990	6.002	37	348.85
3	14.313	10.145	10.145	40	385.71
4	20.562	14.932	14.926	45	448.84
5	27.21	20.207		50	513.96
6	34.16	26.102		55	580.99
7	41.38	32.561		60	649.90
8	48.88	39.526		65	720.66
9	56.65	47.083		70	793.27
10	64.69	55.108		75	867.74
11	72.97	63.087		80	944.09
12	81.50	71.222		85	1022.3
13	90.27	79.392		90	1102.5
14	99.26	87.870		95	1184.7
15	108.5	96.664		100	1268.8
16	117.9	105.67			
17	127.5	114.96			
18	137.2	124.53			
19	147.2	134.55			
20	157.3	144.30			
21	167.6	142.49			
22	178.0	163.50			
23	188.5	174.00			
24	199.2	184.78			
25	210.1	195.83			
26	221.0	207.06			
27	232.1	218.57			
28	243.3	230.29			
29	254.6	242.24			
30	266.1	254.48			
31	277.6	266.45			
32	289.2	278.43			
33	301.0	290.87			
34	312.8	303.32			
35	324.7	315.95			
36	336.7	328.74			

Silverman and Obata[4] have pointed out relationships between the x-ray and electron scattering factors and the diamagnetic nuclear shielding parameter as well as the atomic self-energy. It should be noted that the σ_d(HF) value for Br is 316×10^{-5} which is slightly larger than the interpolated Hartree value used by Silverman and Obata. Also with the electron density functions of Refs. 2 and 3 the integral proportional to the atomic self energy may be evaluated in a closed form yielding for the HF case

$$\int d\mathbf{r}_1\int d\mathbf{r}_2\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}=Z^2\Bigg\{\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{{}^a\gamma_i\,{}^a\lambda_i\,{}^a\gamma_j\,{}^a\lambda_j}{{}^a\lambda_i+{}^a\lambda_j}$$

$$-2\sum_{i=1}^{2}\sum_{j=1}^{M\leq3}\frac{{}^a\gamma_i\,{}^a\lambda_i^2\,{}^b\gamma_j}{({}^a\lambda_i+{}^b\lambda_j)^2}+2\sum_{i=1}^{M\leq3}\sum_{j=1}^{M\leq3}\frac{{}^b\gamma_i\,{}^b\lambda_i\,{}^b\gamma_j\,{}^b\lambda_j}{({}^b\lambda_i+{}^b\lambda_j)^3}\Bigg\}\qquad(3)$$

and for the TFD case

$$\int d\mathbf{r}_1\int d\mathbf{r}_2\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}=Z^2\sum_{i=1}^{3}\sum_{j=1}^{3}\frac{\gamma_i\lambda_i\gamma_j\lambda_j}{\lambda_i+\lambda_j}.\qquad(4)$$

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Anomalies in the NMR and EPR Spectra of XeF_6–HF Mixtures

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We have previously reported that only a single broad line, with T_2 less than T_1, is observed in the F^{19} high-resolution NMR spectrum of XeF_6 in HF.[1] The width and shift of this line depend upon the concentration of XeF_6, whereas the width is independent of magnetic field in the range 14.1×10^3 to 3.75×10^3 G. The single line observed in the proton resonance of the same solutions is narrow and independent of XeF_6 concentration and magnetic field.

The fact that T_2 is less than T_1 in solutions indicates line broadening due to chemical exchange. The concentration-dependent chemical shift of the F^{19} line shows that HF–XeF_6 exchange approaches the fast exchange limit. The width of the single line observed in this case is given approximately by Eq. (1),[2]

$$\frac{1}{T_2'}=\frac{p_A}{T_{2A}}+\frac{p_B}{T_{2B}}+p_A^2p_B^2(\omega_A-\omega_B)^2(\tau_A+\tau_B),\qquad(1)$$

the third term of which represents the broadening due to exchange. If ω_A and ω_B involve chemical shifts, as would be expected for diamagnetic XeF_6 and HF, then the broadening would depend on the strength of the magnetic field, contrary to experiment. The only reasonable conclusion is that there is an additional exchange process which predominantly determines the linewidth and that this process either is slow, or occurs rapidly over a frequency difference which is independent of magnetic field. In either event, one is forced to conclude that a third species is involved in the F^{19} exchange and that this species has an appreciable F^{19} shift.

The presence of a third species in our XeF_6–HF mixture was confirmed by the observation of a resolved EPR spectrum after most of the HF had evaporated. Addition of microliter quantities of HF sharpened