

# Magnetic Susceptibility Measurements Using a Laser-Pendulum Apparatus

Bert Spencer

Castilleja School, Palo Alto, CA 94301

Richard N. Zare

Stanford University, Stanford, CA 94305

The magnetic behavior of materials constitutes one of the most powerful approaches for elucidating the nature of chemical bonding, particularly of the transition metal elements. However, because of the smallness of such effects and the difficulty of making their presence quantitative, this topic is often omitted in teaching. The purpose of this article is to describe an experiment that measures the magnetic susceptibility of a powdered crystalline sample using a simple-to-construct laser-pendulum apparatus in which the sample, suspended by a thread from a pivot, swings back and forth between the poles of a permanent magnet. The thread periodically interrupts a helium-neon laser beam viewed by a photodiode, allowing the period to be measured to high precision with a microcomputer. From a comparison of the periods of different materials the molar susceptibility at room temperature is readily determined. Neither knowledge of the magnetic field strength nor of the nature of its spatial inhomogeneity is required.

Magnetic susceptibility measurements have been reviewed by Selwood (1) with practical considerations appearing in the works of Shoemaker and Garland (2), Brubaker and Stafford (3), Kirschner, Albinak, and Bergman (4), Eaton and Eaton (5), and Loehlin, Kahl, and Darlington (6). The theory of the origin of magnetic dipole moments has been treated mathematically by Figgis (7). This laser-pendulum apparatus takes the place of the more costly and complex Gouy or Faraday balances. It is believed that this experiment introduces the student to many principles of modern physical chemistry: lasers, computer interfacing, quantum chemistry, and the microscopic interpretation of macroscopic phenomena. The laser-pendulum apparatus also serves as an excellent lecture demonstration.

## Relation between Paramagnetic Susceptibility and Unpaired Electrons

When an object is placed in a permanent magnetic field, the field induces in general a magnetic moment in the object. This moment may be in a direction opposing the field and acting to cancel the field strength inside the object (diamagnetism) or in a direction parallel to the field and acting to enhance the magnetic field in the object (paramagnetism).

Let the magnetic field induced in the material be denoted by  $B$  and that outside the material by  $H$ . If a substance is placed in a field of strength  $H$ , then the magnetic induction is given by

$$B = H + 4\pi I \quad (1)$$

The quantity  $I$  is called the intensity of magnetization. The magnetic susceptibility per unit volume is defined by

$$\chi = I/H \quad (2)$$

a dimensionless quantity that represents the intensity of magnetization per unit field strength. We multiply  $\chi$  by the molar volume  $M/\rho$  where  $M$  is the molecular weight (g/mol) and  $\rho$  the density (g/cm<sup>3</sup>) to introduce the quantity

$$\chi_M = (M/\rho)(I/H) \quad (3)$$

called the molar magnetic susceptibility. For a paramagnetic substance  $\chi_M$  is positive and for a diamagnetic substance  $\chi_M$  is negative. The units of  $\chi_M$  are cm<sup>3</sup>/mol. Just as the total molar electric polarizability  $P_e$  can be represented as the sum of the electrical polarizability  $\alpha_e$  and the molecular dipole term  $\mu_e^2/3kT$ , the magnetic analog is

$$\chi_M = N(\alpha_M + \mu_M^2/3kT) \quad (4)$$

where  $N$  is Avogadro's number. Here  $\alpha_M$  is the magnetic polarizability and  $\mu_M$  the magnetic moment.

Most materials have paired electron spins and no magnetic moments. The only contribution to  $\chi_M$  is from  $\alpha_M$ , which is small and negative. Such materials are diamagnetic. However for those materials having unpaired electrons, the positive  $\mu_M^2/3kT$  term far outweighs the negative  $\alpha_M$  term and the substance is paramagnetic. In what follows we neglect the  $\alpha_M$  term in comparison to the  $\mu_M^2/3kT$  term. For molecules containing unpaired electrons, both the spin and orbital angular momenta of the electrons contribute to the observed paramagnetism. However, for most paramagnetic organic and first-row transition metal ions, the orbital contribution is largely "quenched" by the ligands. Thus, to a good approximation it may be assumed that the magnetic moment arises solely from the spins of the unpaired electrons.



An electron has an intrinsic spin of  $s = 1/2$  and acts as a tiny bar magnet with a magnetic moment whose value is twice the magnitude of the spin angular momentum, i.e.,

$$\mu(\text{spin}) = 2|s| = 2\sqrt{s(s+1)} \quad (5)$$

measured in units of Bohr magnetons. If  $S$  is the total spin quantum number, the magnetic moment in Bohr magnetons is

$$\mu(\text{spin}) = 2\sqrt{S(S+1)} \quad (6)$$

that is,

$$\mu(\text{spin}) = \sqrt{n(n+2)} \quad (7)$$

where  $n = 2S$  is the number of unpaired electrons. Upon evaluation of the constants, eq 4 may be rewritten as

$$\mu(\text{spin}) = 2.84\sqrt{\chi_M T} \quad (8)$$

Thus an experimental determination of  $\mu(\text{spin})$  at a temperature  $T$  can be used to deduce the number of unpaired electrons. For octahedral and tetrahedral complexes of transition metal ions, the value of  $n$  can be rationalized in terms of ligand splittings of the  $d$  orbitals into  $t$  and  $e$  levels available for occupancy on a lowest level first basis (7, 8).

### Laser-Pendulum Measurement of the Magnetic Dipole Moment

In the absence of an external field, the period of a simple pendulum is well approximated by

$$\tau = 2\pi(l/g)^{1/2} \quad (9)$$

where  $l$  is the length and  $g$  the gravitational constant. When the simple pendulum containing a paramagnetic sample swings back and forth in an inhomogeneous magnetic field, there is an additional force developed, proportional to  $\chi H^2$ , which always acts to pull the pendulum into the region of highest magnetic field strength at the lowest point in its trajectory, that is, acts the same as gravity. Consequently, the period of the pendulum is shortened. The new period  $\tau'$  can be written as

$$\tau' = 2\pi(l/g')^{1/2} \quad (10)$$

and

$$\begin{aligned} \Delta g &= g' - g \\ &= 4\pi^2 l \left( \frac{1}{\tau'^2} - \frac{1}{\tau^2} \right) \end{aligned} \quad (11)$$

The value of  $\Delta g$  multiplied by the mass  $m$  of the sample is equivalent to an effective weight change

$$\Delta W = m \Delta g \quad (12)$$

We use a standard reference material,  $(\text{CoCl}_2 \cdot 6\text{H}_2\text{O})$ , denoted by the subscript  $S$ , whose molar magnetic susceptibility  $(\chi_M)_S$  is known  $[\chi_M(\text{CoCl}_2 \cdot 6\text{H}_2\text{O}) = 9710.0 \times 10^{-6} \text{ cm}^3/\text{mol}]$ . Then the magnetic moment of the unknown sample is related to the standard reference sample by

$$\mu(\text{spin}) = 2.84 \left[ \left( \frac{\Delta W}{\Delta W_S} \right) \left( \frac{\rho_S}{\rho} \right) \left( \frac{M}{M_S} \right) (\chi_M)_S T \right]^{1/2} \quad (13)$$

Hence the magnetic dipole moment is found by measuring the ratio of  $\Delta W$  to  $\Delta W_S$ .

### Experimental

A sample consisting of approximately 0.200 g of an inorganic substance was suspended from a string of approximately 0.28 m. A plastic cap was epoxied to the string allowing vials to be changed without affecting the system. A 0.5-mW helium-neon laser and silicon photodiode were aligned with the hanging vial. The photodiode was interfaced to an Apple II computer using a Pasco relay box Model 6575 for convenience. The Cross Educational Software pro-

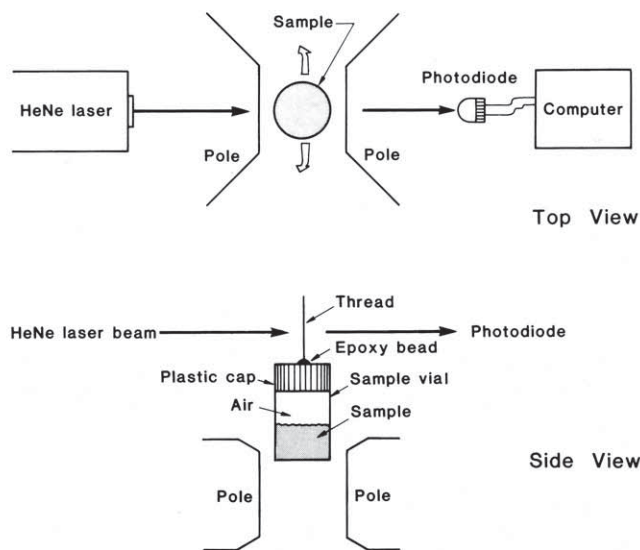


Figure 1. Schematic drawing of the laser-pendulum apparatus.

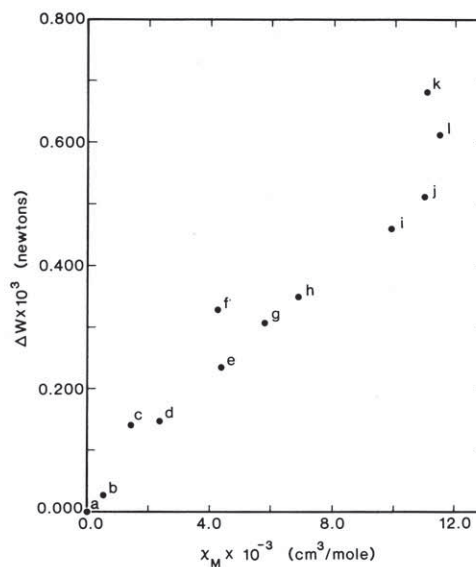


Figure 2. Plot of the observed effective weight change  $\Delta W$  vs. literature values of the molar magnetic susceptibility  $\chi_M$  for 10 different compounds (see the table for identification).

gram LIGHT was modified to record and save period measurements on a disk. The unmodified version could be used as well. A 4.7 kG permanent magnet with a 1-in. pole gap (or one of smaller size) could be moved into place when needed. The sample should sit in the upper quarter of the magnet's gap on the low point of its swing. Figure 1 presents two views of the experimental setup. Small amplitude displacements are best. It was found that the magnet should be moved only once during a set of measurements.

### Results and Discussion

Figure 2 presents a plot of  $\Delta W$  derived from the period of the pendulum vs. the reported molar magnetic susceptibility  $(\chi_M)$  for 10 different compounds. The linearity of the plot shows that the pendulum theory does an adequate job in quantifying the change in the period with different samples. The table compares the experimental value of  $\mu(\text{spin})$  determined for the 10 compounds with their literature values. For the final five discrete octahedral complexes, the table shows,

### Summary of Magnetic Susceptibility Results

Fig. 1 Reference	Compound	$\mu(\text{spin})$ observed	$\mu(\text{spin})$ literature	$n$ calc	$n$ theory <sup>a</sup>
a	ZnCl <sub>2</sub>	0	0 <sup>b</sup>		
a	SnCl <sub>2</sub>	0	0 <sup>b</sup>		
b	CuBr <sub>2</sub>	1.81	1.28 <sup>b</sup>		
c	CuSO <sub>4</sub> ·5H <sub>2</sub> O	1.88	1.88 <sup>b</sup>		
e	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2.88	3.24 <sup>b</sup>		
h	CrCl <sub>3</sub> ·6H <sub>2</sub> O	3.89	4.08 <sup>b</sup>		
i	CoCl <sub>2</sub> ·6H <sub>2</sub> O	4.87	4.87 <sup>b</sup>		
j	Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O	4.99	4.98 <sup>b</sup>		
k	FeSO <sub>4</sub> ·7H <sub>2</sub> O	6.22	5.22 <sup>b</sup>		
a	K <sub>4</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O	0	0 <sup>b</sup>	0	0 (0)
d	K <sub>3</sub> Fe(CN) <sub>6</sub>	2.69	2.4 <sup>b</sup>	1.87	1.60 (1)
f	Ni(NH <sub>3</sub> ) <sub>6</sub> Br <sub>2</sub>	3.20	3.24 <sup>c</sup>	2.35	2.39 (2)
g	K <sub>3</sub> Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	3.80	3.75 <sup>d</sup>	2.92	2.88 (3)
l	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5.49	5.25 <sup>e</sup>	4.58	4.34 (4)

<sup>a</sup> The number in parentheses is the number of unpaired d electrons according to ref 7.

<sup>b</sup> Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC: Boca Raton, FL 1986; E-119-124.

<sup>c</sup> Bose, D. M. Z. *Physik* **1930**, *65*, 677.

<sup>d</sup> Johnson, C. H. *Trans. Faraday Soc.* **1932**, *28*, 845.

<sup>e</sup> See ref. 4.

in addition, the calculated and literature values for the number of unpaired electrons. It would appear that the spin-only expression for the magnetic moment, eq 4, provides only a

fair approximation to the magnetic behavior of these compounds. In particular, values of  $n_{\text{calc}}$  somewhat larger than  $n_{\text{theory}}$  are expected for complexes (d) and (l) owing to the lack of quenching of orbital angular momentum in transition metal ion complexes having  $T$  terms (7).

Although the laser-pendulum technique is not intended to replace existing analytical methods of determining magnetic susceptibilities or moments, its teaching possibilities are significant. Accuracies of up to 5% of the literature values for  $\mu(\text{spin})$  are possible with a little practice and experimental optimization. Simultaneous displays of diamagnetic and paramagnetic period traces on a CRT could be a valuable way of presenting differences in these materials to a large audience.

#### Acknowledgment

We thank Julie A. Tinklenberg for assistance in carrying out the magnetic susceptibility measurements. This work is supported by the National Science Foundation under NSF MDR 84-70336.

#### Literature Cited

- Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience: New York, 1956.
- Shoemaker, D. P.; Garland, C. W. *Experiments in Physical Chemistry*, McGraw-Hill: New York, 1962; pp 289-297.
- Brubacher, L. J.; Stafford, F. E. *J. Chem. Educ.* **1962**, *39*, 574.
- Kirschner, S.; Albinak, M. J.; Bergman, J. G. *J. Chem. Educ.* **1962**, *39*, 576.
- Eaton, S. S.; Eaton, G. R. *J. Chem. Educ.* **1970**, *56*, 170.
- Loehlin, J. H.; Kahl, S. B.; Darlington, J. A. *J. Chem. Educ.* **1982**, *59*, 1048.
- Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1966; Chapter 10, pp 248-292.
- McQuarrie, D.; Rock, P. *General Chemistry*; Freeman: New York, 1984; pp 893-935.