



On the temperature dependence of the exchange interaction
by Craig Edward Zaspel

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF
PHILOSOPHY in Physics

Montana State University

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Abstract:

By assuming an anharmonic intermolecular potential for lattice displacement and an exponential form for the exchange energy, the exchange interaction is shown to be temperature dependent in the paramagnetic region. Bond strengths are taken from known tabulated results and overlap integrals are calculated with Slater-type orbitals so there are no adjustable parameters. Agreement with experimental results of $K_2CuCl_4 \cdot H_2O$ and other layered compounds is shown.

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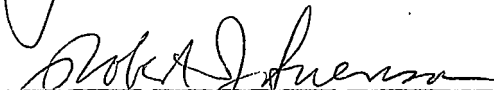
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ABSTRACT

By assuming an anharmonic intermolecular potential for lattice displacement and an exponential form for the exchange energy, the exchange interaction is shown to be temperature dependent in the paramagnetic region. Bond strengths are taken from known tabulated results and overlap integrals are calculated with Slater-type orbitals so there are no adjustable parameters. Agreement with experimental results of $\text{K}_2\text{CuCl}_4 \cdot \text{H}_2\text{O}$ and other layered compounds is shown.

I. AN HISTORICAL INTRODUCTION TO MAGNETISM

The aligning force in magnets was known since the beginning of recorded history, but it was not until the advent of quantum mechanics approximately two thousand years later that this phenomenon was understood. There were numerous attempts to explain magnetism; however, they all relied on some mystical power inherent in the magnet. Theories of the 17th and 18th centuries were related to the ancient Greek theory of magnetic forces. Epicurus¹ explanation relied on the assumption that a magnet had a stream of "seeds" emanating from itself, and attraction was the result of interaction between the seeds and the air around a magnet. The Epicurean theory was not improved until 1644 when Descartes² published Principia Philosophiae. Descartes' theory was somewhat similar, except the particles streaming from the magnet were shaped like screws and they originated from pores near the poles. Since magnets exhibit both attraction and repulsion, there had to be two types of particles--right and left hand screws, and two types of pores--right and left hand nuts. Attraction corresponded to a matched screw and nut, and repulsion corresponded to the interaction of a left hand screw with a right hand nut. This was able to explain all magnetic effects at the time. The state of magnetism before quantum mechanics can best be described by Joyce:³

Universally that person's acumen is esteemed very little perceptive concerning whatsoever matters are being held as most profitable by mortals with sapience endowed to be studied who is ignorant of that which the most in doctrine erudited and certainly by reason of that in them high mind's ornament deserving of veneration constantly maintain when by general consent they affirm that other circumstances being equal by no exterior splendour is the prosperity of a nation more efficaciously asserted than by the measure of how far forward may have progressed the tribute of its solicitude for that proliferent continuance which of evils the original if it be absent when fortunately present constitutes the certain sign of ommipollent nature's incorrupted benefaction.

There was some progress phenomenologically. Weiss⁴ introduced the molecular field or "Weiss" field to explain temperature dependence of the susceptibility. However, the origin of the field remained a mystery until the discovery of electron spin and the Pauli exclusion principle. Finally Heisenberg⁵ applied quantum mechanics to the problem of ferromagnetism and showed that the exchange energy was responsible for magnetic coupling instead of seeds or screws.

The exchange interaction in systems of Fermions is an effect that does not have a analog in classical physics; it comes about from the indistinguishability of Fermions and the Pauli principle. To illustrate the origin of the exchange energy, we will consider two similar atoms A and B separated by a distance R. Using an approach similar to the Heitler-London theory of chemical bonding,⁶ the two-electron wavefunction can be written as the antisymmetrized product of one-electron functions. The one-electron wavefunction is the product of an atomic orbital, φ_A or φ_B for atoms A and B,

and a spin function, α or β for spin up and down. It can easily be shown that the properly antisymmetrized two-electron wavefunctions are:

$$\psi_1 = \frac{1}{\sqrt{2(1-S^2)}} \left\{ \varphi_A(x_1) \varphi_B(x_2) - \varphi_A(x_2) \varphi_B(x_1) \right\} \begin{cases} \alpha(1) \alpha(2) \\ \beta(1) \beta(2) \\ \alpha(1) \beta(2) + \alpha(2) \beta(1) \end{cases}$$

$$\psi_4 = \frac{1}{\sqrt{2(1+S^2)}} \left\{ \varphi_A(x_1) \varphi_B(x_2) + \varphi_A(x_2) \varphi_B(x_1) \right\} (\alpha(1) \beta(2) - \alpha(2) \beta(1))$$

where x_1 and x_2 are the coordinates of electrons 1 and 2. Next these states will be used to calculate the energy for the two-electron system with the Hamiltonian:

$$H = H_1 + H_2 + H_{12}$$

Here H_1 and H_2 are the one-electron terms, and H_{12} is the electron-electron interaction. ψ_1 , ψ_2 and ψ_3 are degenerate; these three states have energy:

$$E_t = \frac{1}{2(1-S^2)} \left\{ 2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_A(1) \varphi_B(2) \rangle - 2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_B(1) \varphi_A(2) \rangle \right\}.$$

The other state is a singlet with energy:

$$E_s = \frac{1}{2(1+S^2)} \left\{ 2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_A(1) \varphi_B(2) \rangle \right. \\ \left. + 2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_B(1) \varphi_A(2) \rangle \right\}.$$

Here, S is the overlap integral, defined by:

$$S = \int \varphi_A(x) \varphi_B(R+x) dx.$$

For reasons which will be immediately apparent, the exchange energy is defined as the difference between the triplet and singlet state energies:

$$E_{ex} = E_t - E_s$$

For the two-electron system this difference is

$$E_{ex} = \frac{1}{1-S^4} \left\{ S^2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_A(1) \varphi_B(2) \rangle \right. \\ \left. - \langle \varphi_A(1) \varphi_B(2) | H | \varphi_B(1) \varphi_A(2) \rangle \right\}.$$

This can be further simplified by explicitly using the one and two-electron parts of the Hamiltonian in the first term above. Now there are terms like

$$\langle \varphi_A(1) \varphi_B(2) | H | \varphi_B(1) \varphi_A(2) \rangle$$

and the integration over the coordinates of electron 2 is trivial; the expression becomes:

$$S \langle \varphi_A(1) | H_1 | \varphi_B(1) \rangle.$$

Doing the same for H_2 , the exchange energy is

$$E_{ex} = \frac{2}{1-S^2} \left\{ - \langle \varphi_A(1) \varphi_B(2) | H_{12} | \varphi_B(1) \varphi_A(2) \rangle \right. \\ \left. - 2S \langle \varphi_A(1) | H_1 | \varphi_B(1) \rangle + S^2 \langle \varphi_A(1) \varphi_B(2) | H | \varphi_A(1) \varphi_B(2) \rangle \right\}.$$

It is now obvious why the above definition was used for the exchange energy; if we had used orthogonal orbitals, the exchange energy

reduces to the ordinary exchange integral

$$E_{ex} = -2J \quad J \equiv \langle \varphi_A(1) \varphi_B(2) | H_{12} | \varphi_B(1) \varphi_A(2) \rangle.$$

For this case, Dirac⁷ showed that the exchange energy depends only on the relative spin orientations and the exchange Hamiltonian could be expressed as a product of spin functions:

$$E_{ex} = -2J \vec{S}_1 \cdot \vec{S}_2.$$

Now we can extend the spin Hamiltonian to the more general problem of nonorthogonal orbitals by defining the exchange constant

$$-J = E_t - E_s$$

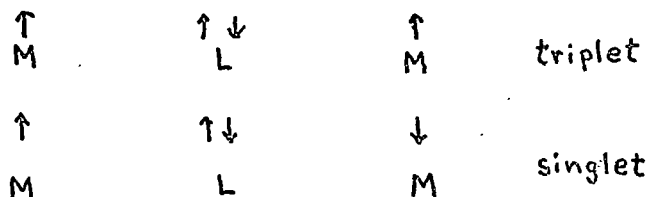
which is the complicated expression that was calculated earlier, and we arrive at the Heisenberg-Dirac-Van Vleck Hamiltonian:

$$H_{ex} = -J \vec{S}_i \cdot \vec{S}_j.$$

Certain observations can be made concerning the sign of J and the magnetic behavior of our two-electron system. First, if J is positive, the parallel spin arrangement will have lower energy; this corresponds to ferromagnetism. For J negative, the antiferromagnetic state will have lower energy. So at least in principle, we can

predict whether a system will be ferromagnetic or antiferromagnetic by calculating $E_s - E_t$. For our two-electron problem, the first term is the ordinary exchange integral; since this is just the self-energy of the overlap charge distribution, the first term in the expression for J is positive. The second term is related to the energy of a single electron bound state, which is negative. The last term can go either way. So even for this simple two-electron system it is very difficult to predict the sign of J because each term in H_{ex} is usually large compared to J , and there is a delicate balance that can go either positive or negative.

Most magnetic systems are considerably more complicated than the previous two-electron problem; usually there is a diamagnetic ligand between the paramagnetic atoms, and the ligand electrons must also be included in the calculation of triplet and singlet state energies. This particular three atom problem is known as superexchange because the magnetic electrons interact over relatively large distances. The exchange constant for superexchange is still the difference between singlet and triplet states; however, the triplet and singlet spin configurations are illustrated below.



It is now necessary to find the energy of both spin configurations, which defines the exchange constant. The calculation is similar to the earlier example except it is a four electron problem, which becomes an immense complication. The most refined calculations of the exchange constant use molecular orbitals for the one-electron functions, and electron correlation is taken into consideration through configuration interaction. But even in these calculations all that can be hoped for is the correct sign for J , so the exchange constant is usually experimentally determined.

When the exchange constant is measured by different methods, which will be discussed later, the possibility that J may be temperature dependent is ignored. The remaining chapters will deal with temperature dependence of the exchange energy. First, experimental methods for measuring the exchange energy will be discussed. The next chapter presents experimental evidence which indicates that the exchange energy is temperature dependent. The final chapters investigate possible mechanisms contributing to the temperature dependence; the theoretical results will then be compared with the experiments presented earlier. The mechanism of primary concern in this work is phonon modulation of the exchange integral. A development of the model for this mechanism comprises chapter five.

II. EXPERIMENTAL DETERMINATION OF THE EXCHANGE ENERGY

All cooperative magnetic properties are determined by the sign and magnitude of J ; epr linewidths, spin-wave dispersion relations, low temperature specific heat, or any other parameter related to cooperative magnetic phenomenon. Therefore, J has to be determined (either experimentally or theoretically) in order to compare magnetic measurements with the Dirac-Heisenberg theory. The exchange constant can be calculated using molecular orbital theory; however, as noted in the introduction, this is very difficult and inaccurate--very much like poorly convergent perturbation theory. For all practical purposes J is determined experimentally from any kind of cooperative magnetic effect. Three methods that are used most often are: low temperature specific heat, susceptibility measurements, and epr linewidth measurements.

A. Spin-wave Specific Heat

Since spin-wave modes are the main contribution to the low temperature specific heat, the expression for the specific heat, C_v , contains J explicitly. The spin-wave contribution to C_v is:

$$C_v = \frac{\partial}{\partial T} \sum_k \hbar \omega_k \langle n_k \rangle ,$$

ω_k is obtained from the spin-wave dispersion relation and $\langle n_k \rangle$ is the Bose-Einstein distribution. Employing the following three approximations: k is small, the only spin-spin interaction is expressed as the Heisenberg Hamiltonian, and the sum is converted to an integral over k ; it can straightforwardly be shown that the specific heat is⁹:

$$C_v = \frac{15}{4} \zeta\left(\frac{5}{2}\right) k_B \left(\frac{k_B}{4\pi J S a^2} \right)^{3/2} T^{3/2}$$

for a simple cubic lattice with lattice constant a . This method is useful for determination of J in the low temperature region, $T < T_c$, because spin-wave excitations are the main contribution to the specific heat.

B. Curie and Neel Temperature

A method to directly obtain J is the determination of the Weiss temperature for ferromagnets or the Neel temperature for antiferromagnets. The Weiss Temperature θ is defined by the Curie-Weiss law for temperature dependence of the susceptibility.⁹

$$\chi = \frac{C}{T - \theta}$$

where C is a constant, z is the number of nearest neighbors and

$$\theta = \frac{S(S+1)}{3k_B} z J.$$

Thus J can be obtained from the intercept of a χ^{-1} vs T curve.

Similarly, for an antiferromagnet, the susceptibility is given by⁹ :

$$\chi = \frac{C}{T + T_N}$$

where $T_N = \frac{|J|S(S+1)}{3k_B} Z.$

C. EPR Linewidths

1) Spin-Spin Interaction

We can get J for high temperature from the width of exchange narrowed epr lines. The two interesting cases are: the effect of exchange on the relative separation of two resolved resonance lines with different g values, and exchange narrowing of a single resonance line. The first case has been treated by Anderson¹⁰ for two lines symmetrically spaced $\pm \omega_0$ from an arbitrary center. The exchange interaction tends to bring two lines together, and the shift from ω_0 is given by:

$$\Delta\omega = \mp \omega_e \sqrt{\frac{\omega_0^2}{\omega_e^2} - 1}.$$

If ω_0 can be determined from a preferred orientation of the external field, then the exchange energy, $J \approx \hbar \omega_e$ can be obtained from a measurement of $\Delta\omega$. This method was used to obtain J for the compound $K_2CuCl_4 \cdot 2H_2O$, which will be discussed in the next chapter.

The effect of J on the width of a single line can be illustrated by the following problem: Consider an array of spins in an external magnetic field; the Hamiltonian is expressed as three terms:

$$H = H_z + H_d + H_e,$$

where each term is defined by

$$H_z = g\beta H \sum_i S_i^z$$

$$H_d = \sum_{i>j} \frac{g^2\beta^2}{r_{ij}^3} \left\{ \vec{S}_i \cdot \vec{S}_j - 3(\vec{S}_i \cdot \hat{r}_{ij})(\vec{S}_j \cdot \hat{r}_{ij}) \right\}$$

$$H_e = -J \sum \vec{S}_i \cdot \vec{S}_j.$$

The sum in H_e is over nearest neighbor pairs. An external field of the form:

$$H_1^x \cos \omega t$$

will induce transitions between the Zeeman levels. For infinite temperature the absorption line for these transitions is given by the expression¹¹:

$$I(\omega) = \int_{-\infty}^{\infty} \langle S_x(t) S_x(0) \rangle e^{i\omega t} dt,$$

and $S_x(t)$ can be calculated from the Heisenberg equation,

$$i\hbar \frac{d}{dt} S_x = [H, S_x].$$

Since S_x commutes with the exchange Hamiltonian, H_e is not included explicitly in the equation of motion. However, H_e does not commute with H_d , and H_d has a time dependence given by:

$$i\hbar \frac{d}{dt} H_d = [H_{ex}, H_d] ,$$

or in other words, the dipole interaction is modulated by the exchange energy. Using an explicit form for the matrix element of $H_d(t)$ and assuming $\omega_e \gg \omega_d$, Anderson and Weiss¹¹ have shown that the resonance linewidth is given approximately by:

$$\Delta\omega \propto \frac{\omega_d^2}{\omega_e}$$

where ω_d^2 is the second moment of the resonance line, and $\omega_e = J/\hbar$. This expression for $\Delta\omega$ can change by a factor of about 1.5 depending on how H_d is modulated by the exchange interaction.

To arrive at the above result for $\Delta\omega$ it was assumed that $\omega_e \gg \omega_d$ and the form of modulation was a Gaussian random function. As shown by Richards¹², this is equivalent to assuming the spin correlation function has a time dependence

$$\langle S_x(t) S_x(0) \rangle \propto \cos \omega t e^{-t/\tau_2} ,$$

and evaluation of the integral for $I(\omega)$ using this correlation function results in a Lorentzian lineshape given by

$$I(\omega) \sim \frac{\omega \Delta \omega}{(\omega - \omega_0)^2 + \Delta \omega^2}$$

where $\omega_0 = g\beta H$, $\Delta \omega = 1/\tau_2$, and τ_2 is the spin-spin correlation time, or the lifetime of the excited Zeeman state. In the absence of a spin-lattice interaction, the exchange constant can be obtained from a knowledge of the epr linewidth and second moment. The temperature dependence of J may then be extracted from the linewidth at different temperatures.

It should also be mentioned that Kubo and Tomita¹³ did a perturbation series expansion for the spin correlation function, and calculated the linewidth at finite temperature.

2) Spin-Lattice Interaction

One contribution to the linewidth that was ignored because the spin-phonon interaction did not appear in the Hamiltonian is spin-lattice relaxation. There are many mechanisms--that will be considered later--which couple the spin system and the lattice, but as an example consider the Waller¹⁴ process: A spin in the state $M_S = \frac{1}{2}$ makes a transition to the $M_S = -\frac{1}{2}$ state by interaction with a phonon of energy $g\beta H$. A transition rate W can be calculated and from this the lifetime of the $M_S = \frac{1}{2}$ state is related to W by $\tau = \frac{1}{W}$.

What type of perturbations will cause spin flips? The exchange Hamiltonian commutes with S_z^2 , so phonon modulation of J will not contribute to W . Next consider the dipole-dipole interaction:

$$H_0 = \sum_{i \neq j} \frac{g^2 \beta^2}{r_{ij}^3} (3 \cos^2 \theta_{ij} - 1) \left\{ \frac{1}{4} (S_i^+ S_j^- + S_i^- S_j^+) - S_i^z S_j^z \right\}$$

$$H_1 = \sum_{i \neq j} \frac{g^2 \beta^2}{r_{ij}^3} \frac{3}{2} \sin \theta_{ij} \cos \theta_{ij} \left\{ (S_i^z S_j^+ + S_i^+ S_j^z) e^{-i\phi_{ij}} + (S_i^z S_j^- + S_i^- S_j^z) e^{i\phi_{ij}} \right\}$$

$$H_2 = \sum_{i \neq j} \frac{g^2 \beta^2}{r_{ij}^3} \frac{3}{4} \sin^2 \theta_{ij} \left\{ S_i^+ S_j^+ e^{-2i\phi_{ij}} + S_i^- S_j^- e^{2i\phi_{ij}} \right\}$$

$$H_d = H_0 + H_1 + H_2$$

The selection rules are $\Delta M_s = 0$ for H_0 which does not result in spin flips, whereas for H_1 and H_2 $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$; therefore, for this process a finite T_1 is the result of modulation of H_1 and H_2 . It is interesting to note that when H_1 and H_2 are included in the spin-spin correlation function, the linewidth is increased by a factor of $10/3$ which makes $\Delta\omega$ agree much better with experimental linewidths. This mechanism for spin-lattice relaxation and the $10/3$ effect¹¹ originate from the same Hamiltonian; sometimes they

are even given the same name.

Two relaxation processes contribute to the observed linewidth: the spin-spin relaxation with its characteristic T_2 , and the spin-lattice interaction which has a corresponding spin-lattice relaxation time, T_1 . In order to extract J from the epr linewidth, it is necessary to determine how $\Delta\omega$ depends on $1/T_1$ and $1/T_2$. The simplest case has a characteristic bell-shaped resonance curve, and the widths are given approximately by $\Delta\omega_1 \propto \frac{1}{T_1}$ and $\Delta\omega_2 \propto \frac{1}{T_2}$. Using the suggestion of Bloembergen, Purcell, and Pound¹⁵, the assumption will be made that the observed resonance line is the sum of two lines at ω_0 each of which have widths $\Delta\omega_1$ and $\Delta\omega_2$. The resulting line, $Y(\omega)$, not necessarily Gaussian, is:

$$Y(\omega) = I_1 \exp\left\{-\ln 2 \left(\frac{\omega - \omega_0}{\Delta\omega_1/2}\right)^2\right\} + I_2 \exp\left\{-\ln 2 \left(\frac{\omega - \omega_0}{\Delta\omega_2/2}\right)^2\right\}.$$

The width of $Y(\omega)$ is obtained from the expression relating the linewidth and the second moment-- $\Delta\omega^2 \propto c \langle \omega^2 \rangle$ ¹⁶; c is a constant that depends on the particular lineshape, $\langle \omega^2 \rangle$ is the second moment of $Y(\omega)$ given by:

$$\langle \omega^2 \rangle = \frac{1}{A} \int_{-\infty}^{\infty} (\omega - \omega_0)^2 Y(\omega) d\omega$$

where A is the area under the resonance line:

$$A = \int_{-\infty}^{\infty} Y(\omega) d\omega.$$

The integration can easily be done and the linewidth for both relaxation mechanisms is:

$$\Delta\omega \sim \sqrt{\Delta\omega_1^2 + \Delta\omega_2^2 - \Delta\omega_1 \Delta\omega_2}.$$

If $T_1 \gg T_2$, $\Delta\omega$ is approximately:

$$\Delta\omega \approx \frac{1}{T_2} + \frac{1}{2T_1}$$

and frequently the second term can be neglected completely so J is obtained in that case from the results of reference (10).

For the case when T_1 is not large, different spin-lattice relaxation mechanisms besides the Waller process must be looked at. A very good review of different mechanisms is given in reference (16), and each will be considered briefly here.

The Waller process results in a relaxation time given by $\frac{1}{T_1} \sim H^2 T$. A typical T_1 is 10 sec, and a typical T_2 is 10^{-9} sec so this process is too long to contribute to the linewidth.

Next consider a spin-phonon collision where the energy loss of a phonon is $g\beta H$. This is the two-phonon Raman process which

was also treated by Waller¹⁴ in 1932. The temperature dependence of T_1 can be obtained for two cases. For low temperatures, $k_B T \ll \hbar \omega_0$, and $\frac{1}{T_1} \sim T$; for high temperature, $k_B T \gg \hbar \omega_0$, and $\frac{1}{T_1} \sim T^2$.

A typical Θ_0 is 100°K so $1/T_1$ usually goes as something between T and T^2 for this process. In the high temperature approximation, T_1 is still about 10 sec at 300°K which is still much greater than T_2 .

A shorter T_1 can come from modulation of the ligand field¹⁷ which sets up an oscillating electric field as a perturbation. This perturbation will only have a direct effect on the crystal field splitting of orbital states, and the spin-phonon coupling is a second order effect that comes from spin-orbit coupling. For the one-phonon direct process non-Kramers and Kramers ions, which have integral and half-integral spin respectively, are investigated separately. The ground state of a non-Kramers ion can split in a crystalline field of low enough symmetry. Modulation of the Stark field then affects the spin through the spin-orbit interaction. With appropriate calculations, the relaxation time is shown to have a field and temperature dependence¹⁷:

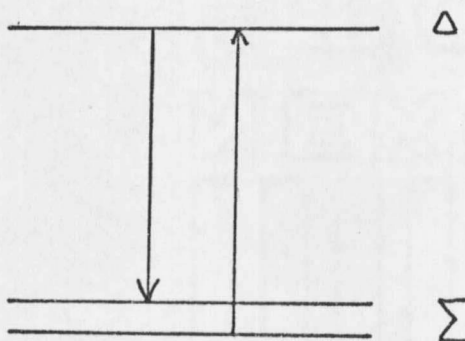
$$\frac{1}{T_1} \sim H^2 T.$$

At first glance it appears as if phonon modulation will not affect the ground state of a Kramers ion. However, Kronig¹⁸ has shown that there are matrix elements due to the interaction of the Kramers state and the Stark field in the presence of an external magnetic field. For this case:

$$\frac{1}{T_1} \sim H^4 T.$$

A non-Kramers ion will have a T_1 of about 10^{-3} sec and a Kramers ion has a T_1 of 1 sec for this process, which is still long compared to T_2 .

In 1961 Orbach¹⁹ was able to account for the anomalously short relaxation times by a process that is essentially an indirect transition between two Kramers states.

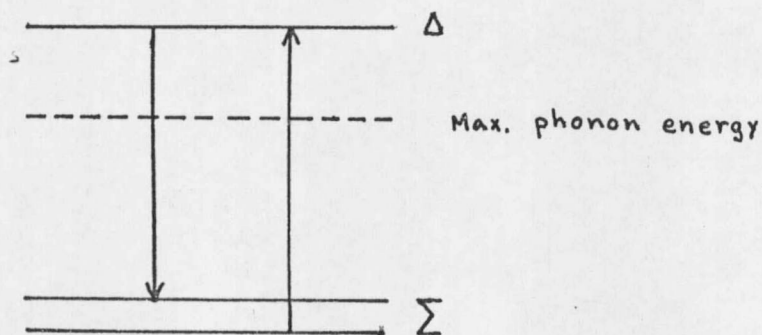


Σ is a Kramer's doublet, Δ is an excited orbital state, and the two steps of the transition are indicated of the diagram. For this process, the relaxation time is:

$$\frac{1}{T_1} \sim \exp\left(-\frac{\Delta}{k_B T}\right)$$

subject to the condition $\Delta \gg k_B T$. T_1 is extremely temperature dependent since $\Delta \gg k_B T$; also T_1 can be the same order of magnitude as T_2 .

There is also a two-phonon Raman process where the spin-phonon interaction comes from modulation of the ligand field. Two types of mechanisms are considered on the following diagram.



The first process arises from quadrupole transitions between the two non-Kramers Σ states. The second process is similar to the two-phonon Orbach process except it requires absorption and emission of

a virtual phonon because the excited state, Δ , is outside of the phonon continuum. Both mechanisms have a temperature dependence given by:

$$\frac{1}{T_1} \sim T^7,$$

and a typical T_1 is 10^{-8} sec which is also comparable with T_2 .

By looking at the magnetic field and temperature dependence of the epr linewidth, it should--at least in principle--be possible to determine if $\Delta\omega$ is related to T_1 or T_2 . For example, if the linewidth is linear in temperature and quadratic in external magnetic field, then the Waller process is probably the main relaxation mechanism. If it is then determined that the temperature dependence of $\Delta\omega$ is from spin-lattice relaxation, it is then necessary to extrapolate the linewidth versus T curve to 0°K where T_1 is large; then $\Delta\omega$ is directly related to T_2 . However, it must be emphasized that the exchange energy cannot be obtained from the low temperature linewidth by using Anderson's or Kubo and Tomita's equation, since it is an infinite temperature approximation. There are two complications that arise in the theory of finite temperature epr linewidths: First, there is a difference in population of the Zeeman levels. Second, the spin correlation functions have a temperature dependence. The theory of exchange narrowed resonance lines at finite temperature

has been done by Richards¹² for spin correlation functions with an exponential time dependence. For high temperature, $kT \gg \omega_e$, strong exchange narrowing, $\omega_e \gg \omega_0$, and ignoring the temperature dependence of certain correlation function, the linewidth at finite temperature is given approximately by

$$\Delta \omega \sim \frac{\omega_d^2}{\omega_e \chi T} .$$

Measurement of the quantity $\chi T \Delta \omega$ will now yield ω_d^2 / ω_e , from which the exchange energy can be extracted if the second moment of the resonance line is known.

III. EXPERIMENTAL EVIDENCE FOR TEMPERATURE DEPENDENCE OF EXCHANGE

In the previous chapter we have discussed methods used to determine the exchange energy at different temperatures: epr linewidth measurements for the paramagnetic region, susceptibility measurements for the Curie and Néel temperatures, and low temperature specific heat measurements below the Curie and Néel temperature. If these methods yield different exchange energies, this is an indication that the exchange energy may be temperature dependent. For example, the low temperature specific heat yields a J at approximately 1 or 2 °K, and J at room temperature can be obtained from the epr linewidth at this temperature. Indeed, certain transition metal salts do show strong evidence for temperature dependence of the exchange energy. One of the most striking examples is $K_2CuCl_4 \cdot 2H_2O$. This compound has two inequivalent Cu chains, and the different chains have g values g_1 and g_2 . For exchange energies less than⁹

$$J \lesssim \frac{1}{2} (g_1 - g_2) \beta H,$$

there will be two resolved resonance lines. If g_1 and g_2 are known, J can be estimated from the above expression for the particular magnetic field where both lines coalesce. Okuda and Date²⁰ used this method to obtain J for $K_2CuCl_4 \cdot 2H_2O$ between 200 and 300°K.

At high frequencies the linewidth is¹⁰

$$g_{Av} \beta \Delta H \simeq \frac{1}{8J} \{ (g_1 - g_2) \beta H \}^2.$$

Kennedy, Choh, and Seidel²¹ obtained J in this way between 77°K and 200°K. The temperature dependence of J for $K_2CuCl_4 \cdot 2H_2O$ from reference (21) is shown in Figure I. It can be seen that J changes by a factor of five between 77°K and room temperature; also if $J(T)$ is extrapolated to low temperature, J is approximately 0.30°K which

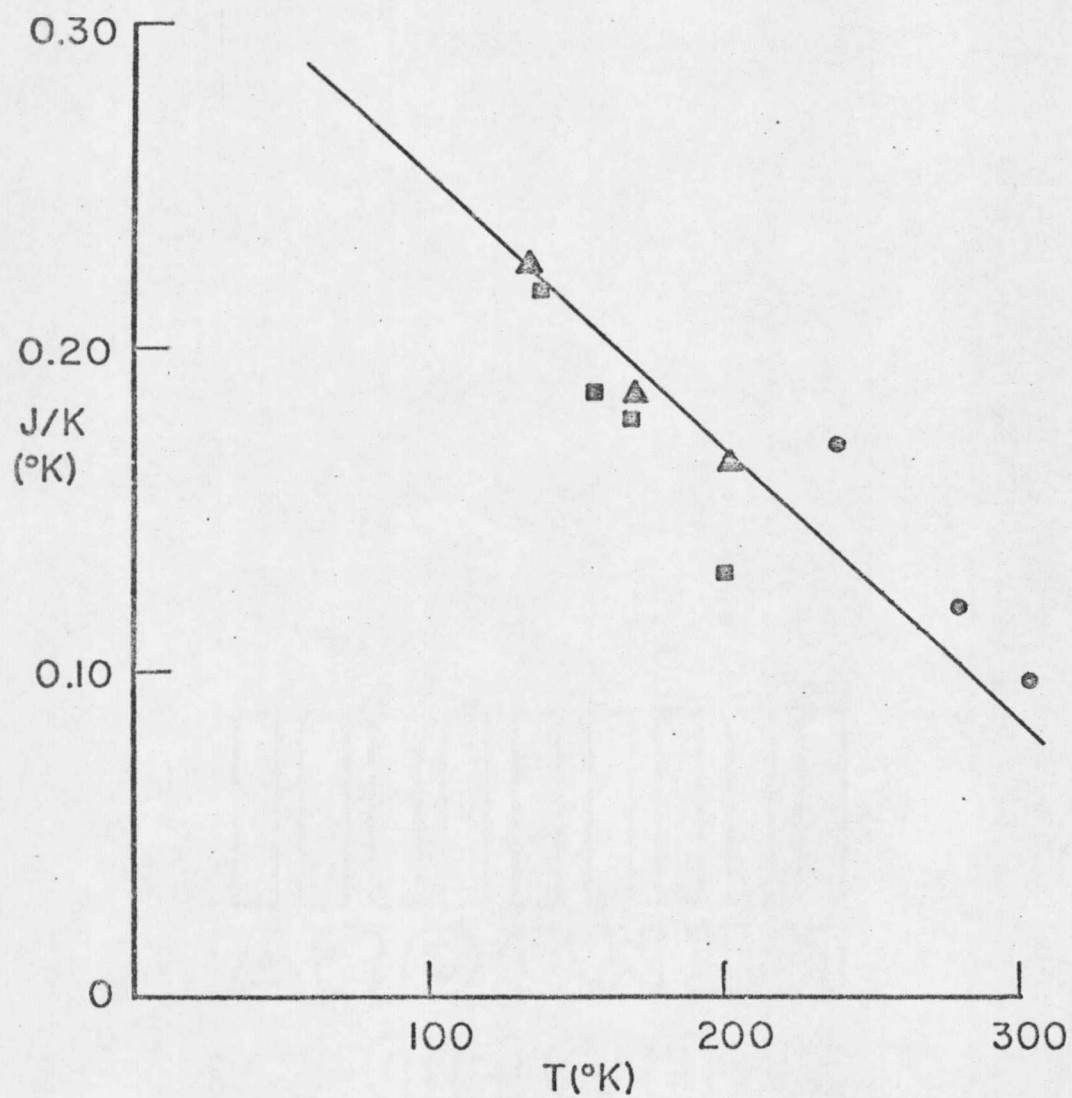


FIGURE I

Temperature dependence of the exchange interaction in $K_2CuCl_4 \cdot 2H_2O$. Circles are from the data of Okuda and Date. The triangles and squares are from epr linewidths at 35 and 65 GHz.

agrees very well with J obtained from low temperature specific heat measurements²². Another class of compounds which appears to have a temperature dependent J are the layered structures $(C_nH_{2n+1}NH_3)_2CuCl_4$. These compounds have an extremely exchange narrowed epr linewidth which exhibits a linear temperature dependence²³ illustrated in Figure II. Seehra and Castner²⁴ explained this temperature dependence for the layered structure $Cu(HCOO)_2 \cdot 4H_2O$ by phonon modulation of the anti-symmetric exchange interaction. However, for this interaction to be non-zero, there must be spin-orbit coupling and there cannot be inversion symmetry with respect to the magnetic ions²⁵.

There are compounds that do not have an antisymmetric exchange interaction, but still have a temperature dependent linewidth. The magnetic ions in K_2CuF_4 are centrosymmetric²⁶; however, the linewidth still has a linear temperature dependence²⁷. Furthermore, the compounds, $(C_nH_{2n+1}NH_3)_2MnCl_4$ also have temperature dependent linewidths²⁸, and since Mn^{++} is an S-state ion there cannot be a spin-orbit interaction. The paramagnetic dimethyl sulfoxide, $CuCl_2 \cdot 2DMSO$ also has a temperature dependent linewidth²⁹ although it is not known if the dependence is linear because the measurements were only made at 77°K and 300°K. However, isotropy of the g-value indicates that spin orbit coupling is not large enough to explain the temperature dependence. Clearly--at least for $K_2CuCl_4 \cdot 2H_2O$, K_2CuF_4 ,

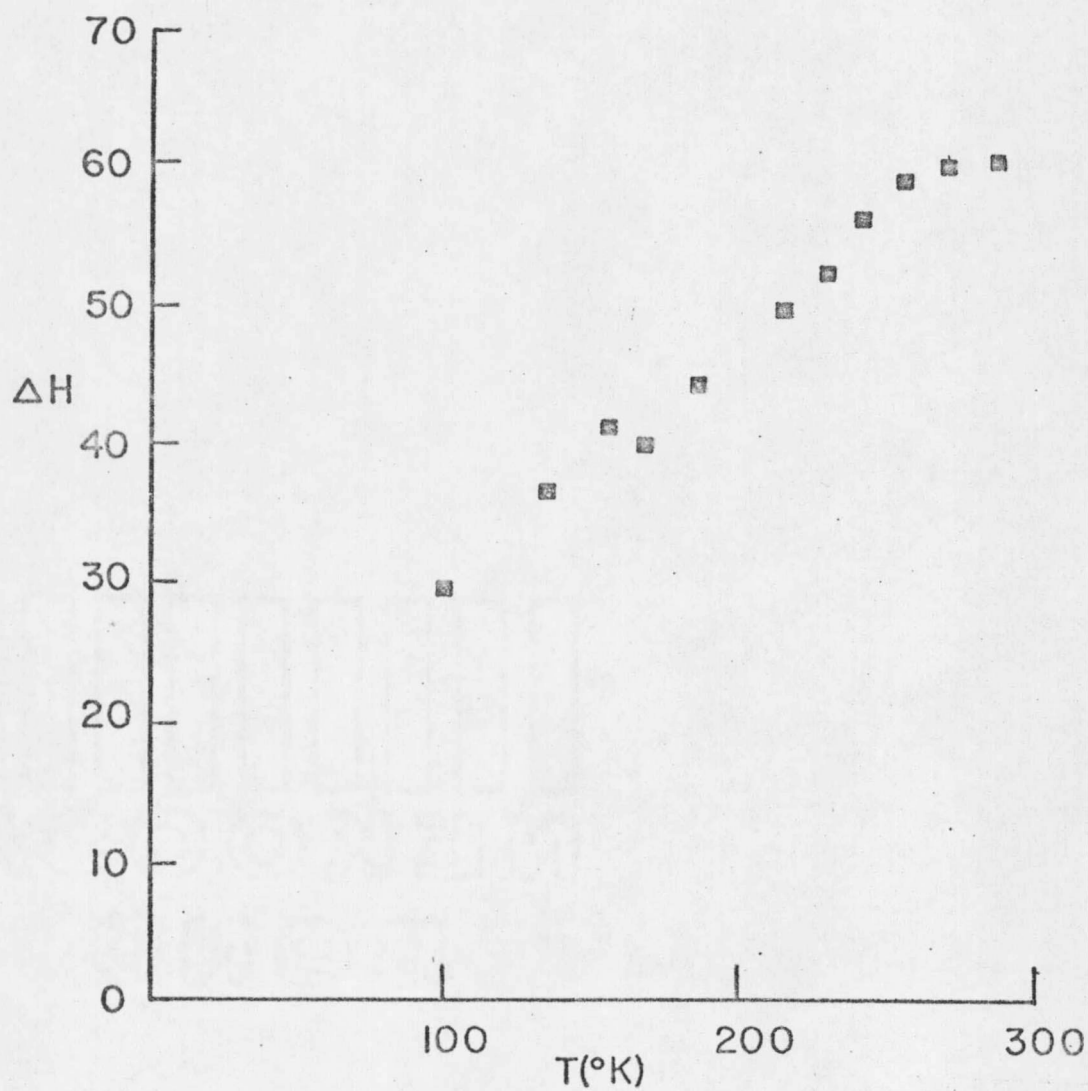


FIGURE II

EPR linewidth versus temperature for $n\text{-propylammonium (nP-NH}_3)_2\text{CuCl}_4$.

and $(C_n H_{2n+1} NH_3)_2 MnCl_4$ must be some other mechanism responsible for the temperature dependent linewidth.

Could this peculiar effect arise from spin-lattice relaxation? If the spin-phonon interaction is the principal source of broadening, the linewidth is approximately:

$$\Delta \omega \sim \frac{1}{T_1}$$

Each mechanism contributing to T_1 will be considered separately.

The Waller process has a temperature dependence given by

$$\Delta \omega \sim H^2 T,$$

and it can be eliminated for two reasons: First, as previously noted, a typical relaxation time is 10 sec which is too large by many orders of magnitude. Second, the linewidth has a field dependence; this is not observed experimentally.

Also, the two-phonon Raman process does not result in a linear temperature dependence, and the relaxation time is still about 10 sec.

Next we will consider modulation of the ligand field. This process can be disregarded for the Mn^{++} salts and $CuCl_2 \cdot 2DMSO$ immediately because there is no spin-orbit interaction to connect the spin and orbital states. For the other compounds, the one-phonon Raman process gives a linewidth that goes as T^7 so it can

certainly be disregarded. Only the two-phonon Orbach process is left; this has a temperature dependence:

$$\Delta\omega \sim \exp\left(-\frac{\Delta}{T}\right).$$

Using Δ approximately 10^3 K which is a typical crystal field splitting for transition metal ions, it is seen that between 100° K and room temperature the linewidth changes by a factor of 10^4 . Experimentally, the linewidth changes by roughly a factor of two in this range, so the Orbach process can be ruled out also.

Apparently, the anomalous temperature dependent linewidth must be from some other mechanism than phonon modulation of the anti-symmetric exchange interaction and spin-lattice relaxation. Since all the spin-lattice relaxation mechanisms were eliminated, the relaxation time must be the result of spin-spin interaction, and for this case the linewidth is given by:¹²

$$\Delta\omega \sim \frac{\omega_d^2}{\omega_e \chi T}.$$

Apparently there are three terms in the linewidth that can have a temperature dependence: the second moment, ω_d , which is related to two-spin correlation functions; the χT factor; and the exchange energy. A more detailed investigation later will show that the

temperature dependent linewidth for antiferromagnetic Mn^{++} salts can be explained by the temperature dependent correlation functions in ω_d , ω_e and χT . However, since the temperature dependent linewidth for K_2CuF_4 still cannot be explained by any of the above processes, it is proposed that this effect is the result of a temperature dependent exchange energy as in $K_2CuCl_4 \cdot 2H_2O$. In the following chapters, a circumspect investigation of the Heisenberg Hamiltonian will reveal possible mechanisms for this temperature dependence.

IV. TEMPERATURE DEPENDENCE OF THE SPIN CORRELATION FUNCTION

If the exchange energy is indeed temperature dependent, the first logical step is to calculate the thermal average of the Heisenberg Hamiltonian over spin states. The source contributing to the temperature dependence is spin correlation; this effect is taken into consideration by calculating the ensemble average of the Heisenberg Hamiltonian:

$$\langle H_{ex} \rangle = \langle -J \vec{S}_i \cdot \vec{S}_j \rangle.$$

The angular brackets indicate that an ensemble average is taken over all spin states; for example:

$$\langle \vec{S}_i \cdot \vec{S}_j \rangle = \frac{1}{Z} \sum_{\mu \nu r} e^{-E_{\mu}/kT} \langle \mu | S_i^r | \nu \rangle \langle \nu | S_j^r | \mu \rangle,$$

where Z is the partition function, and E is the energy of the particular state. The next obvious step then is the derivation of the static correlation function, $\langle S_i(0) \cdot S_j(0) \rangle$, which is usually done with Green's functions.

The statistical Green's function is particularly useful for this type of problem because it contains the time correlation and commutation properties of two operators; in this case S_i and S_j .

For these two operators, the definitions of the retarded and advanced Green's functions are:

$$G_r(t, t') = -i \Theta(t - t') \{ \langle S_i(t) S_j(t') \rangle - \langle S_j(t') S_i(t) \rangle \}$$

$$G_a(t, t') = -i \Theta(t - t') \{ \langle S_i(t) S_j(t') \rangle - \langle S_j(t') S_i(t) \rangle \},$$

or in more compact notation

$$G_r(t, t') = \langle\langle S_i(t); S_j(t') \rangle\rangle_r$$

$$G_a(t, t') = \langle\langle S_i(t); S_j(t') \rangle\rangle_a.$$

In principle, it should be possible to obtain all the information about an operator by finding the Green's function defined in terms of the operator. With this in mind, we can use the Heisenberg

equation to generate an equation of motion for $G(t, t')$:

$$i \frac{dG}{dt} = \delta(t-t') \langle [S_i(t), S_j(t')] \rangle + i \langle\langle \frac{d}{dt} S_i(t); S_j(t') \rangle\rangle.$$

The Heisenberg equation can be used to find $\frac{d}{dt} S_i(t)$ also; doing this the equation of motion becomes:

$$i \frac{dG}{dt} = \delta(t-t') \langle [S_i(t), S_j(t')] \rangle + i \langle\langle [S_i(t), H(t)]; S_j(t') \rangle\rangle.$$

So $G(t, t')$ is expressed in terms of a higher order Green's function that involves a commutator of one operator and the Hamiltonian. Similarly, this higher order Green's function can be found in terms of a still higher order function, namely:

$$\langle\langle [S_i(t), [S_i(t), H(t)]]; S_j(t') \rangle\rangle,$$

and an infinite chain of Green's functions can be formed. The problem now reduces to finding an approximation that will truncate the chain and give a set of coupled differential equations that can be solved for $G(t, t')$. Usually it is assumed that the Fourier components of the spin operators are independent, then the

higher order Green's function is

$$\langle\langle S_{k'}(t) S_{k''}(t); S_k(t') \rangle\rangle \simeq \langle S_{k'}(t) \rangle \langle\langle S_{k''}(t); S_k(t') \rangle\rangle.$$

This is the random phase approximation. This set of equations is usually solved by Fourier transforming the Green's function

$$G(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(t) e^{-iEt} dt,$$

as well as any higher order Green's functions, and we arrive at a set of linear equations. $G(E)$ can easily be found and $G(t)$ is then its Fourier transform; however, a problem arises here: $G(E)$ has poles on the real E axis. It is necessary either to move the poles off the axis, or analytically continue $G(E)$ in the complex E plane, in order to evaluate the Fourier transform. Using the following boundary conditions for the time Green's function,

$$G_r(t) = 0 \quad \text{for } t < 0$$

$$G_a(t) = 0 \quad \text{for } t > 0,$$

Zubarev³⁰ has shown that $G_a(E)$ and $G_r(E)$ can be analytically continued to form a single function

$$G(E) = \begin{cases} G_r(E) & \text{Im } E > 0 \\ G_a(E) & \text{Im } E < 0 \end{cases}$$

with a branch cut along the real axis; also, $G(E)$ satisfies the same equation of motion as $G_r(E)$ and $G_a(E)$.

Next it is necessary to relate $G(E)$ to the correlation function. First, however, the problem is simplified if we Fourier transform the correlation function

$$\langle S_i(t) S_j(0) \rangle = \int_{-\infty}^{\infty} I(E) e^{iEt} dE.$$

When the ensemble average is written out explicitly, it can be shown that the other correlation function is³⁰

$$\langle S_j(0) S_i(t) \rangle = \int_{-\infty}^{\infty} I(E) e^{E/KT} e^{iEt} dE;$$

$I(E)$ is known as the spectral intensity, probably because it is related to the epr lineshape by the equation in chapter II. Now, employing the above boundary conditions, along with the relations involving the spectral intensity, the Green's function is related to $I(E)$ by

$$G(E+i\epsilon) - G(E-i\epsilon) = -i \left(e^{E/kT} - 1 \right) I(E)$$

for E real.

The Green's function theory of ferromagnetism has been done by many workers. However, we will use the results of Tahir-Kheli and Ter Haar³⁰, which relates the two-spin correlation function to the magnetization. From this result it is then possible to determine the static correlation function from the temperature dependent susceptibility.

Tahir-Kheli and Ter Haar used the Green's function

$$\langle\langle S_i^+; S_j^- \rangle\rangle,$$

and the Hamiltonian

$$H = -g\beta H/\hbar \sum_i S_i^z - \sum_{i,j(\text{nn})} J \vec{S}_i \cdot \vec{S}_j$$

to obtain the following expression for the correlation function:

$$\langle S^- S^+ \rangle = 2\hbar \langle S^z \rangle \Phi(1/2).$$

$\Phi(1/2)$ is related to the Bose-Einstein distribution for spin 1/2,

$$\Phi(1/2) = \frac{1}{N} \sum_k \left(e^{E_k/kT} - 1 \right)^{-1},$$

and E_k is a pole of the Green's function given by

$$E_k = g\beta H + 2\hbar \langle S^z \rangle (J(0) - J(k)).$$

It is now possible to relate the correlation function to the susceptibility. From the definition of χ ,

$$\chi = \frac{M_z}{H_z}$$

we have the following expression:

$$\chi = \frac{Ng\beta \langle S^- S^+ \rangle}{2H_z \Phi(1/2)}.$$

Next it is necessary to determine $\Phi(1/2)$ as a function of temperature. There is an explicit temperature dependence in the denominator of the exponent, as well as an implicit temperature dependence in the magnetization term, $\langle S^z \rangle$. This last term will be obtained from the high temperature expansion of $\Phi(1/2)$:

$$\Phi(1/2) = \frac{1}{2t_0} \left(1 - \frac{\langle S^z \rangle}{\hbar t_0 \tau} + \frac{z+1}{z} \left(\frac{\langle S^z \rangle}{\hbar t_0 \tau} \right)^2 + \dots \right)$$

where z is the coordination number, and the parameters t_0 and τ are defined by

$$t_0 = \tanh\left(\frac{1}{2} g \beta H / kT\right)$$

$$\frac{1}{\tau} = \frac{J(0) \hbar^2}{kT} .$$

Also we know that $\Phi(1/2)$ can be expressed in terms of $\langle S^z \rangle$;

$$\Phi(1/2) = \frac{1}{2\langle S^z \rangle} \left(\frac{\hbar}{2} - \langle S^z \rangle \right) ,$$

so both of the above equations can be solved for $\langle S^z \rangle$ in terms of t_0 which yields for high temperature

$$\langle S^z \rangle = \frac{\hbar}{2 + 1/t_0} .$$

Now t_0 is expanded in a power series, and in the high temperature approximation only the first term is kept--

$$t_0 \simeq \frac{1}{2} g \beta H / kT .$$

Finally the high temperature approximation for $\Phi(\nu_2)$ is obtained by putting the above expression for $\langle S^z \rangle$ into $\Phi(\nu_2)$, and we arrive at the following relation between the susceptibility and the correlation function,

$$\chi T = g^2 \beta^2 N \langle S^- S^+ \rangle / 2 k T$$

The temperature dependence of the two-spin correlation function can now be obtained directly from measurements of susceptibility for a particular compound. This experiment has been done for the $(C_n H_{2n+1} NH_3)_2 CuCl_4$ series²³; however, we are only interested in the high temperature region, $kT \gg J$; and in this case χ is approximated by the series expansion³²,

$$\frac{\chi T}{C} = 1 + 2 \frac{J}{kT} + \dots$$

The temperature dependence of the correlation function is now

$$\langle S^- S^+ \rangle \sim 1 + 2 \frac{J}{kT} + O\left(\frac{J}{kT}\right)^2$$

and the exchange energy is roughly related to temperature by the following expression

$$\langle H_{ex} \rangle \sim -J \left(1 + 2 \frac{J}{kT} \right).$$

For $K_2CuCl_4 \cdot 2H_2O$ $\frac{J}{k}$ is $0.30^\circ K$ and the above result has a negligible temperature dependence from $100^\circ K$ to $300^\circ K$. Clearly, there must be some other mechanism that is responsible for the temperature dependence of the exchange energy.

V. TEMPERATURE DEPENDENCE OF THE EXCHANGE CONSTANT

In the previous chapter, only the correlation function was considered in a search for the mechanism responsible for the temperature dependence of exchange, and the assumption was made that the exchange constant was indeed constant. If J is temperature dependent, the correlation function is more complicated and the exchange energy is then:

$$\langle H_{ex} \rangle = \langle - 2 J \vec{S}_i \cdot \vec{S}_j \rangle.$$

Using the approximation that J and the correlation function are uncorrelated, the exchange energy becomes:

$$\langle H_{ex} \rangle = - \langle J \rangle \langle \vec{S}_i \cdot \vec{S}_j \rangle.$$

So, at least for the compounds of the previous chapter, the effect that is observed experimentally must be from a temperature dependent J .

There are at least two processes which will give the exchange constant a temperature dependence. The first process is the result of a breakdown of the Born-Oppenheimer approximation. In this case, there will be radiationless transitions to excited molecular orbitals,

which will alter the energy of the singlet and triplet states, and temperature dependence will result because the transition rate is related to the phonon occupation number. The second process is phonon modulation of the exchange integral.

A. Breakdown of the Born-Oppenheimer Approximation

As an example of this first process, consider the CuCl_4 ion with D_{2d} symmetry. The magnetic electron is in a molecular orbital that can be expressed as a linear combination of atomic orbitals

$$B_2 = \alpha d_{xy} + \delta p,$$

where p is a sum of ligand p orbitals that have the appropriate symmetry. Also from reference (33) it is known that $\delta < \alpha$. The lowest energy charge transfer band is a transition from a lower degenerate orbital E ,

$$E = \beta(d_{xz} + d_{yz}) + \epsilon p, \quad \beta < \epsilon$$

to an orbital of B_2 symmetry, which leaves a hole in E . Since $\delta < \alpha$ and $\beta < \epsilon$, the effect of this transition is to move the magnetic electron closer to the ligand, hence the name "charge transfer". Therefore, this transition will increase the overlap of p and d functions which in turn will increase the exchange interaction between the two CuCl_4 complexes. This mechanism will increase the exchange

energy with increasing temperature, which is not the experimentally observed effect. However, the frequency of this charge transfer band is about 10^{15} or 10^{16} Hz and the vibrational frequency is about 10^{12} Hz, so the Born-Oppenheimer approximation is very good for the transition metal salts that exhibit a temperature dependent-exchange energy, and this process will no longer be considered.

B. Phonon Modulation of the Exchange Integral

Phonon modulation of the exchange integral was suggested by Harris and Owen³⁴ as a possible explanation of the temperature dependence of the epr linewidths of $(\text{NH}_4)_2\text{Ir,PtCl}_6$. Also, Griffiths³⁵ expanded the exchange interaction in phonon operators to explain the anomalous temperature-independent spin-lattice relaxation time of diphenyl picryl hydrazyl (DPPH). Recently, Kennedy et. al.²¹ proposed that this mechanism may be responsible for the temperature dependent exchange energy in $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$.

To calculate an explicit temperature dependence of J, we will consider a MX_4 dimer, where M is metal and X is a ligand. If M is Cu, there is an unpaired electron in one of the metal type molecular orbitals of the MX_4 complex, and the intermolecular exchange interaction between the magnetic electrons can be represented by a Heisenberg Hamiltonian. In this case, J does not have a simple form, but it is related to integrals like³⁶:

$$I = \iint \psi_M^a(x_1) \psi_L^b(x_2) H \psi_M^b(x_1) \psi_L^a(x_2) dx_1 dx_2 ,$$

where a and b refer to the two complexes, and x_1 and x_2 are the coordinates of the magnetic electrons. These integrals can be evaluated very roughly by using the Mulliken approximation³⁷:

$$I = \overline{H} S^2,$$

where $\overline{H}$ is an average value for the two-electron Hamiltonian and S is the overlap of appropriate atomic orbitals. Assuming that the exchange energy is proportional to an overlap integral by the approximation, J has the form:

$$J(\delta R) \approx J_0 e^{-\lambda \delta R}$$

for a displacement, δR of the distance between the MX_4 complexes. This functional form for $J(\delta R)$ was used by Seehra and Castner²⁴ to obtain the antisymmetric exchange constant, and it was also used by Griffiths³⁵ because this particular form lends itself very well to expansion in terms of phonon operators.

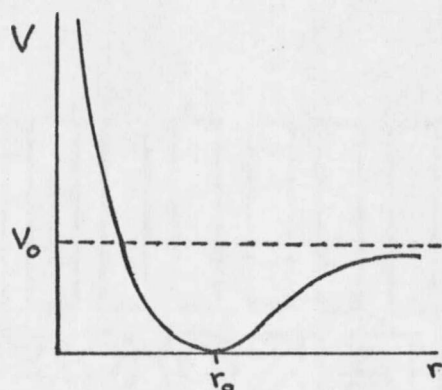
Now that the expression $J(\delta R)$ is justified, the following method will be used to calculate $\langle J \rangle$ as a function of temperature. $\langle J \rangle$ is a thermal average over the vibrational states of the dimer, so first these states will be found by assuming some form for the intermolecular potential. In this model, each CuX_4 complex vibrates as a

single unit; we will also consider relative motion within a single complex, which will affect the oscillators' reduced mass. Next, the matrix elements of the operator, $J(\delta R)$, are calculated for these vibrational states. Griffiths³⁵ has calculated these matrix elements approximately by expanding $J(\delta R)$ in the series

$$J(\delta R) = J_0 \left(1 - \lambda \delta R + \frac{1}{2} \lambda^2 (\delta R)^2 + \dots \right)$$

and Richards³⁸ considered the problem of temperature dependence by finding the thermal average of the operators $(\delta R)^2$ and $(\delta R)^3$ in the above expression. However, for typical values of the parameters, the expansion parameter, $\langle \lambda \delta R \rangle$, is approximately one, so the Taylor's expansion is not justified. Therefore, it is necessary to find matrix elements of the operator, $e^{-\lambda \delta R}$; then it will be a simple matter to do a thermal average over the vibrational states to obtain $\langle J \rangle$. The dimer model is then compared with the crystal by employing the Einstein approximation.

The intermolecular potential one could use anything that has the form indicated below, but a Morse function is convenient because the intermolecular potential V_0 is tabulated and it bears reasonable resemblance to reality. The Morse function is given by



$$V(r) = V_0 \left(1 - \exp\left(-\frac{r-r_0}{a}\right) \right)^2$$

Here, V_0 is the bond dissociation energy, r_0 is the bond length, and a is a constant that is related to the anharmonicity and frequency. We are only interested in the region where

$$\delta R \ll r_0$$

so the potential can be written as

$$V(\delta R) \simeq V_0 + V_2(\delta R)^2 + V_3(\delta R)^3$$

where V_2 and V_3 are proportional to the second and third derivatives of the Morse function evaluated at the equilibrium bond length, r_0 .

To calculate the vibrational states, the last term in the series expansion for $V(\delta R)$ will be treated as a perturbation,

$$H' = V_3(\delta R)^3.$$

The unperturbed state is just the harmonic oscillator wavefunction, and addition of the perturbation results in the anharmonic oscillator problem. To second order, the anharmonic state is then:

$$|n\rangle = |n\rangle + \sum_m \left\{ \frac{\langle m|H'|n\rangle}{E_n^0 - E_m^0} \left(1 - \frac{\langle n|H'|n\rangle}{E_n^0 - E_m^0} \right) |m\rangle + \sum_k \frac{\langle k|H'|m\rangle \langle m|H'|n\rangle}{(E_n^0 - E_m^0)(E_n^0 - E_k^0)} |k\rangle \right\}$$

E_n^0 and $|n\rangle$ are the unperturbed harmonic oscillator energies and states, first sum is over all states except $|n\rangle$, and the second sum is over all states except $|k\rangle$ and $|n\rangle$.

The matrix element

$$I_n = \langle n|J(\delta R)|n\rangle$$

is evaluated in Appendix I, and since H' is third order in R , it can immediately be seen that I_n is the sum of the following terms:

$$\langle n+1|J(\delta R)|n+3\rangle, \langle n-1|J(\delta R)|n+3\rangle, \langle n-1|J(\delta R)|n+1\rangle,$$

$$\langle n-3|J(\delta R)|n-1\rangle, \langle n-3|J(\delta R)|n+1\rangle, \langle n|J(\delta R)|n+6\rangle,$$

$$\langle n|J(\delta R)|n+2\rangle, \langle n|J(\delta R)|n-2\rangle, \langle n|J(\delta R)|n-6\rangle,$$

each of which can be integrated. The matrix element I_n also contains matrix elements connecting states differing by more than 6. However, to be consistent with second order perturbation results, matrix elements of the form $\langle m|J|n \rangle$ for $|n-m| > 6$ are dropped. The term, $V_4(\delta R)^4$ is not considered because the first order correction to I_n is approximately γ smaller than the contribution from $V_3(\delta R)^3$.

With each of these terms evaluated, the thermal average of $\langle J(\delta R) \rangle$ is:

$$\langle J(\delta R) \rangle = \sum_n P_n I_n.$$

P_n is the probability of the system being in the n^{th} vibrational state;

$$P_n = \frac{e^{-E_n^0/kT}}{\sum_s e^{-E_s^0/kT}}.$$

Using $E_s^0 = (s + \frac{1}{2})\hbar\omega$, P_n can be written in closed form

$$P_n = e^{-\hbar\omega/kT} (e^{\hbar\omega/kT} - 1)^{-1} e^{-\hbar\omega n/kT},$$

which will be more convenient.

Before we proceed further, it is possible to eliminate the parameter a , by comparing the Morse function with the exchange energy.

Since the bond energy is indeed closely related to the exchange energy, it is reasonable to assume that both have the same exponential form. This implies that $a \propto 1/\lambda$, so now it is only necessary to obtain λ , V_0 , and the reduced mass of the oscillator.

Here it is convenient to define the dimensionless parameter

$$Y = \frac{\lambda \hbar}{2 \sqrt{2 m V_0}},$$

or using the second derivative of the Morse potential

$$Y = \frac{\lambda^2 \hbar}{2 m \omega},$$

Y can also be expressed in terms of frequency.

Next a value of λ has to be calculated for the appropriate metal-ligand bond. This will be done by comparing the exponential part of a M-L overlap integral

$$S = \int \psi_M(x) \psi_L(x+R) dx$$

with $e^{-\lambda \delta R}$. We are only interested in the radial part of S , so Slater type orbitals (STO) will be used for ψ_M and ψ_L . The STO for an atomic orbital is:

$$\psi = N r^{n^*-1} e^{-\frac{Z^*}{n^*} r},$$

where r is measured from the nucleus of the atom in atomic units, N is a normalization constant, n^* is an effective quantum number, and z^* is the effective nuclear charge defined by

$$Z^* = Z - S$$

where s is the screening constant. Both n^* and s are calculated from the rules in reference ³⁹, which are reproduced here:

(1) For $n = 1, 2, 3, 4, 5$ n^* is given the following values
 $n^* = 1, 2, 3, 3.7$.

(2) Electrons are divided into the groups

1s

2s, 2p

3s, 3p

3d

4s, 4p

4d

For any group of electrons, s has the following contributions

- (a) Zero for any electron outside the group.
- (b) An amount of .35 for each other electron in the group unless the group is 1s, then .30 is used.
- (c) An amount of .85 for each electron in a shell with total quantum number less by one, and 1.0 for each electron further in; if the group is d or f, an amount of 1.0 for every electron further in.

As an example, we will find Z^* for a d electron of Cu(II), which has

the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$. The shielding constant for each group inside the d group is:

1s:	2(1.0)
2s2p:	8(1.0)
3s3p:	8(1.0)
3d:	8(.35)

This yields a screening constant of 20.8, and the corresponding Z^* is 5.2. The procedure is used for other transition metals and halides, and the results are in table 1.

Using these orbitals, S can be integrated, but this is not necessary if we just want the exponential part, which is:

$$\exp \frac{1}{2} \left(-\frac{Z_M^*}{n_M^*} - \frac{Z_L^*}{n_L^*} \right)$$

in units of inverse Bohr radii.

TABLE I
EFFECTIVE QUANTUM NUMBERS, NUCLEAR CHARGE, AND OVERLAP
PARAMETERS FOR CERTAIN METALS AND LIGANDS

M	L	z_M^*	n_M^*	z_L^*	n_L^*	λ
Cu	Cl	9	3	5.75	3	
Cu	F	9	3	4.85	2	5.4
Mn	Cl	4.4	3	5.75	3	5.4
Mn	F	4.4	3	4.85	2	3.9

Z^* and n^* are used in the above expression to obtain S for different M-L bonds which immediately yields a value for the overlap parameter, λ also indicated in table I.

The bond energy V_o is not known for most of the compounds listed in the previous chapters. However, the bond energy can be estimated from the postulate of the geometric mean, which was proposed by Pauling⁴⁰. For a heteronuclear diatomic molecule, this postulate relates the bond energy in Kcal/mole to the homonuclear bond energy of each atom by the relation:

$$D(M-L) = (D(M-M)D(L-L))^{1/2} + 30(x_M - x_L)^2.$$

$D(M-M)$ and $D(L-L)$ are the bond energies of the metal and ligand homonuclear diatomic molecules, and the last term accounts for the extra bond energy resulting from partial ionic character of the bond if there is a difference in electronegativity, x_M and x_L , of the metal and the ligand. The homonuclear bond strength and electronegativity can be obtained from standard references⁴¹; these quantities, as well as $D(M-L)$, are included in table II.

The next step is to relate the calculated bond energy to the bond energy of the compounds. This will be done by comparing the metal-ligand bond length of the particular compound to a calculated bond length corresponding to the above energy. For example, if the bond length corresponding to the geometric mean bond

TABLE II
HOMONUCLEAR BOND STRENGTHS ELECTRONEGATIVITY, AND BOND
STRENGTHS FOR METALS AND LIGANDS

Bond	D(M-M)	D(L-L)	x_M	x_L	D(M-L)
Cu-Cl	47.0 Kcal/m	57.9	1.9	3.0	89.0
Cu-F	47.0	37.7	1.9	4.0	78.5
Mn-Cl			1.5	3.0	70.0
Mn-F			1.5	4.0	82.0

energy is less than the metal-ligand bond length of the compound, then the postulate of the geometric mean probably gives an estimate of the bond energy that is too high, and a suitable correction will have to be made.

To be consistent, the bond lengths are calculated from an equation relating to the covalent radii and the electronegativity difference⁴⁰:

$$R(M-L) = r_M + r_L - c |x_M - x_L| \quad c \approx .06 \text{ \AA}$$

in units of Å. $R(M-L)$ is indicated in table III for different metal-ligand bonds, and they are compared with some of the measured bond lengths of different compounds. Apparently the calculated bond lengths are too short, which means that the calculated bond energy is too large, and it has to be adjusted to agree with the longer bonds. This is done with an equation proposed by Pauling⁴⁰:

$$R(n) = R(1) - 0.60 \log n .$$

Here n is the bond number defined by the following relation between the bond energies for two bond numbers, n and 1:

$$V(n) = n V(1)$$

TABLE III

COVALENT RADII AND BOND DISTANCES FOR METAL-LIGAND BONDS

Bond	r_M	r_L	$x_M - x_L$	$R(M-L)$	$R(\text{measured})$
Cu Cl	1.35 ^o A	.99	1.1	2.27	2.79 $(\text{NH}_4)_2\text{CuCl}_4$
Cu F	1.35	.63	2.1	1.85	2.08 K_2CuF_4

$R(n)$ and $R(1)$ are the bond lengths for the corresponding bond numbers. Now if $V(1)$ and $R(1)$ are known, the bond strength, $V(n)$, can be calculated for any bond length, $R(n)$. These quantities are in table IV: $V(1)$ is the heteronuclear bond energy from table II; n is calculated from Pauling's equation relating the bond lengths (in table III) to the bond number; and $V(n)$ is the bond strength for the particular measured bond length. This bond energy, $V(n)$ is used along with λ and the reduced mass of the particular oscillator m to arrive at the parameter Y .

An estimate of Y is now made for $K_2CuCl_4 \cdot 2H_2O$. This compound can be thought of as an aggregate of K ions, $CuCl_2 \cdot H_2O$ molecules, and Cl ions. The oscillator we will consider is two weakly bonded $CuCl_2 \cdot 2H_2O$ molecules which has a reduced mass of $(1.4)10^{-22}$ gm; λ obtained from table I for the Cu-Cl bond is $(5.0)10^8$ cm⁻¹; and V_0 from table IV is $.612(10)^{-12}$ erg. These numbers correspond to a Y of about 0.02, or if Y is defined by

$$Y = \frac{\lambda^2 \hbar}{2 m \omega}$$

this mass and λ result in a vibrational frequency of $(6.8)10^{12}$ Hz.

Families of curves for $\langle J \rangle$ verses temperature are illustrated in Figures III, IV, and V. In each family the mass is a constant, and λ and V_0 are variables in the parameter Y . Figures III, IV, and V are for the CuCl_4 , CuF_4 dimers, and the Cu-F-Cu molecule respectively. For small Y , roughly between 0.01 and 0.005, $\langle J \rangle$ has little temperature dependence; however, the exchange integral becomes very temperature dependent as Y is increased to 0.04 or 0.05. The experimental results of Kennedy et al. also on Figure III, agree very well with the $\langle J \rangle$ curve for $Y=0.02$.

It is also interesting to note that $\langle J \rangle$ becomes extremely temperature dependent in a relatively small range of Y . This is probably why strongly bonded transition metal salts such as MnF_2 and $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ show no indication of a temperature dependent exchange energy. This is discussed in greater detail in the next chapter.

TABLE IV

BOND NUMBERS AND BOND STRENGTHS FOR METAL LIGAND BONDS

Bond	n	$V(1)$	$v(n)$
Cu-Cl	0.10	6.12×10^{-12} erg	0.612×10^{-12} $K_2CuCl_4 \cdot 2H_2O$
Cu-Cl	0.18	6.12	1.1 $(NH_4)_2CuCl_4$
Cu-F	0.608	4.90	2.98 K_2CuF_4

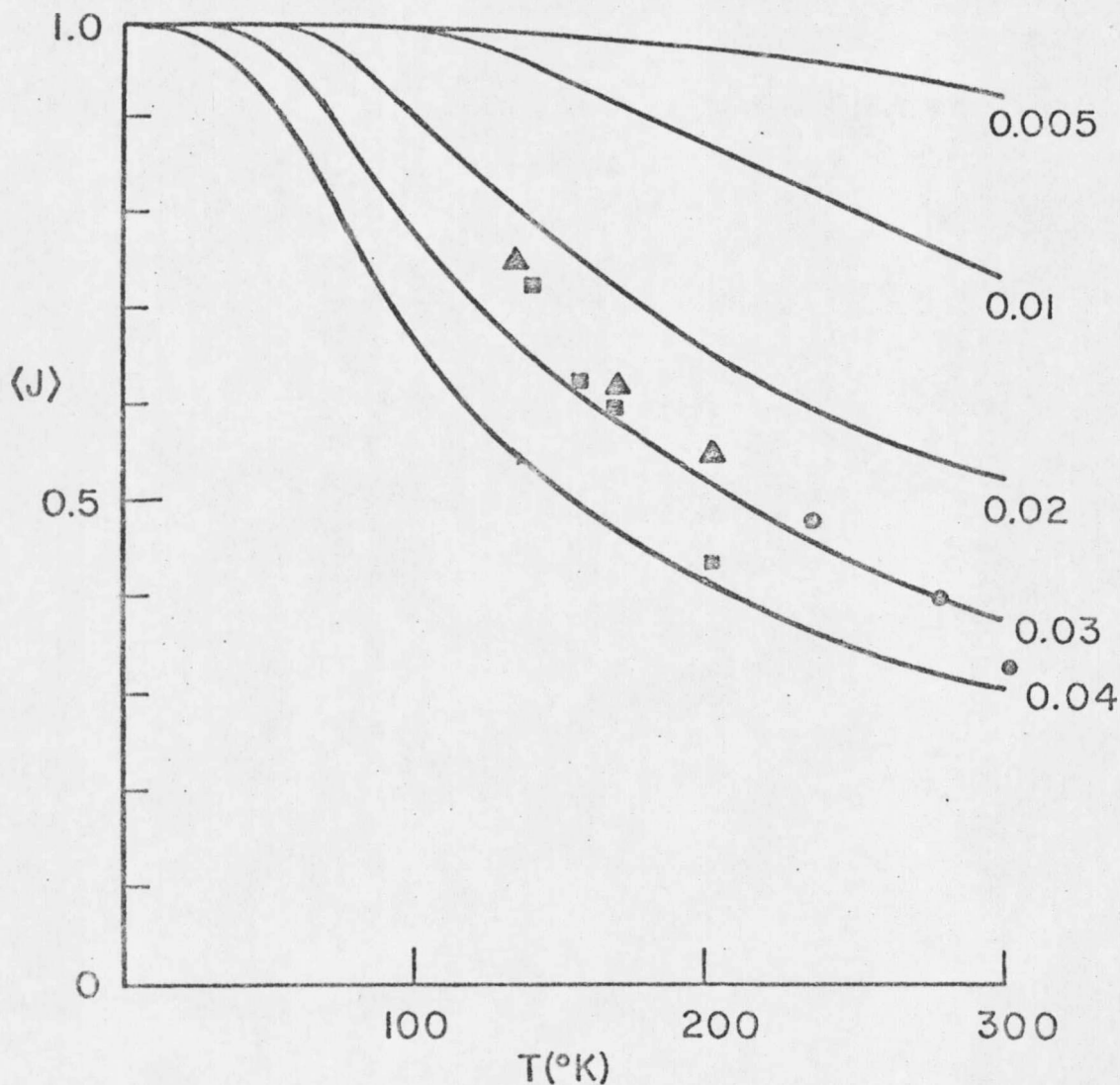


Figure III

The exchange energy J versus temperature for CuCl_4 . Solid lines are for $Y = \frac{\lambda \hbar}{2\sqrt{2mV_0}}$ where λ is related to the overlap integral and V_0 is the bond energy for the dimer. Experimental points are those for $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$. All curves are normalized to one at 0°K .

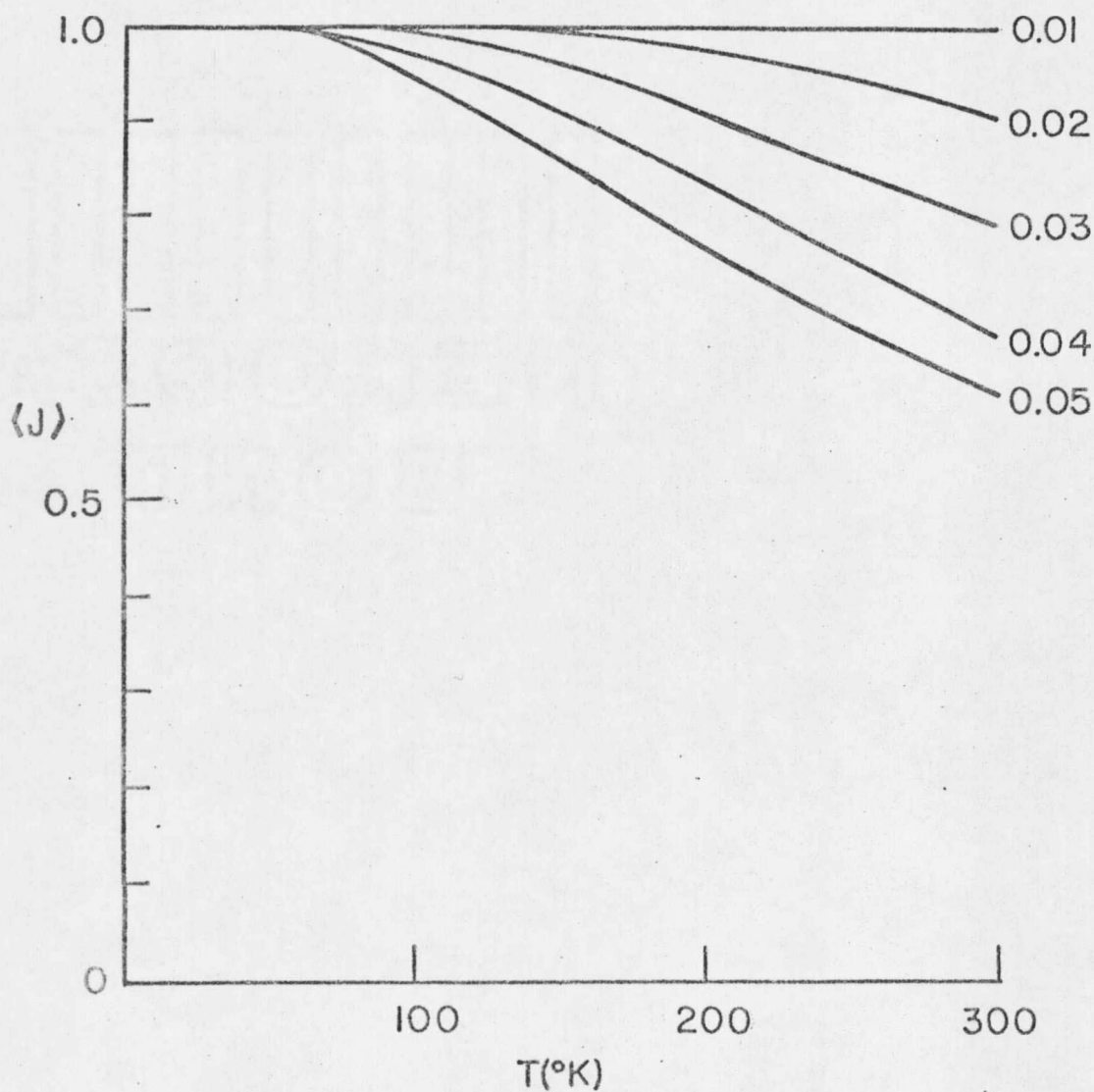


Figure IV

The exchange energy J versus temperature for CuF_4 . Solid lines are for $Y = \frac{\lambda \hbar}{2\sqrt{2mV_0}}$ where λ is related to the overlap integral and V_0 is the bond energy for the dimer. All curves are normalized to one at 0°K

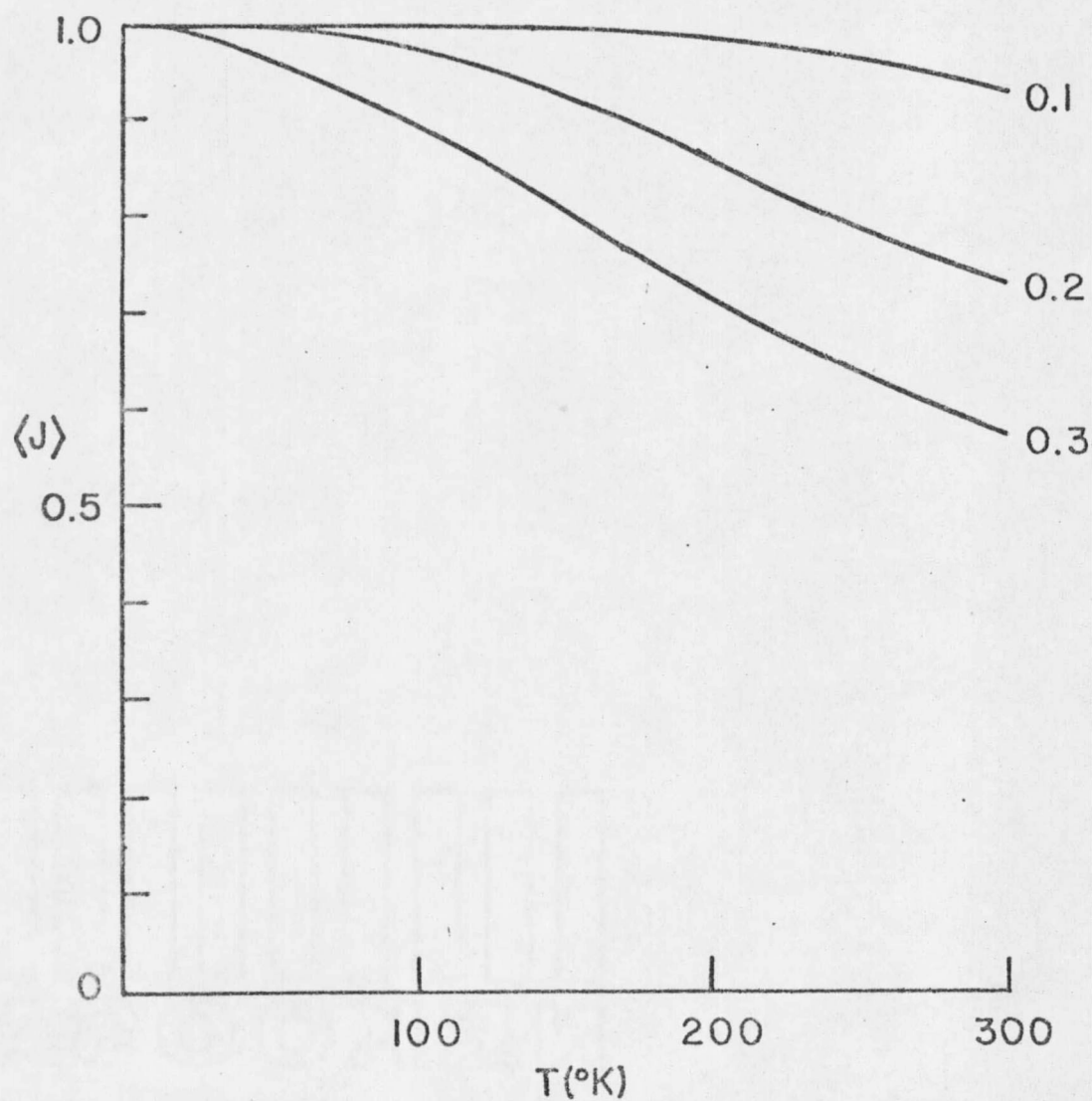


Figure V

The exchange energy J versus temperature for the Cu-F-Cu molecule. Solid lines are for $Y = \frac{\lambda \hbar}{2\sqrt{2mV_0}}$ where λ is related to the overlap integral and V_0 is the bond energy for the dimer. All curves are normalized to one at 0°K.

VI. TEMPERATURE DEPENDENCE OF EPR LINEWIDTHS

From the preceding chapters there are three mechanisms which may result in a linearly temperature dependent linewidth: spin-lattice relaxation, which was eliminated for all compounds we considered; temperature dependence of the spin correlation functions, which affects the quantities ω_d , ω_e , and χT in the linewidth expression; and temperature dependence of the exchange constant, J .

Before we determine how a temperature dependent J affects the linewidth, it is necessary to investigate the effects of spin correlation in the above quantities. First consider the susceptibility. Since we are only interested in the high temperature region, the χT factor is approximated by the series expansion

$$\frac{\chi T}{C} = 1 + 2 \frac{J}{kT} + \dots$$

This in turn gives the following temperature dependence to the linewidth for $J \ll kT$: $\Delta\omega = \frac{\omega_d^2}{\omega_e} \left(1 - 2 \frac{J}{kT}\right)$. J is approximately 10°K or less for all the compounds listed earlier so it appears as if the temperature dependence of χT is a negligible affect in the range from 70°K to room temperature.

There is no simple method for finding the correlation function's contribution to the temperature dependence of ω_d and ω_e ; each system must be treated separately. Richards¹² used Anderson's¹¹ theory extended to finite temperature and Bonner and Fisher's⁴² spin correlation functions to calculate the temperature dependent linewidth of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$. The calculated epr linewidth has little temperature dependence above 20°K which agrees very well with the experimental results of Date⁴³. However, it seems as if this mechanism will not give an appreciable temperature dependence to the linewidth unless the correlation functions have a large temperature dependence in the region of interest, which is not the case for all the compounds listed earlier.

The original expressions for linewidth were derived on the assumption that the correlation function had an exponential time dependence. However, it is now known that for long times, the time dependence is determined by the classical diffusion equation. In other words, for d dimensions

$$\lim_{t \rightarrow \infty} \langle S(t) S(0) \rangle \sim |t|^{-d/2}$$

For 3 dimensions the time dependence goes as $t^{-3/2}$ which is not critically different from the exponential time dependence in Anderson's theory.

Recently Richards⁴⁴ has shown that spin diffusion in lower dimensional systems will modify linewidth theory sufficiently to explain the temperature dependence in two dimensional Heisenberg antiferromagnets. In addition to ω_d , ω_e , and KT , the diffusion constant also has a significant temperature dependence. There is no closed form expression for the linewidth as a function of temperature; however, the theory agrees very well with the data for K_2MnF_4 . It must be emphasized that this theory only predicts the correct temperature dependence for two-dimensional antiferromagnets. For the two-dimensional ferromagnets, K_2CuF_4 and $(C_nH_{2n+1}NH_3)_2CuCl_4$, spin diffusion theory predicts the wrong slope of the $\Delta\omega$ versus T curve at high temperature.

From the preceding discussion, we know that there is at least one compound, K_2CuF_4 , which does not fit any of the theories outlined earlier: spin-lattice relaxation, temperature dependence of the correlation functions, spin diffusion, or phonon modulation of the antisymmetric exchange interaction. In the last chapter it was shown that the exchange constant is inversely related to temperature for certain parameters, and since $\Delta\omega$ is proportional to $1/J$, this effect can explain the temperature dependence of linewidth very well.

First we will look at K_2CuF_4 . The main difference between this compound and other layered structures is in the symmetry of the bonds.

All planar Cu-F bond lengths in K_2CuF_4 are equal, whereas the $(C_nH_{2n+1}NH_3)_2CuCl_4$ series has two different bond lengths in the plane. Therefore, a more realistic model for the harmonic oscillator states is the Cu-F-Cu molecule instead of the CuF_4 dimer. This molecule has a reduced mass of $(0.13)10^{-22}$ gm, and from the tables of the previous chapter, λ is $(5.4)10^8$ cm⁻¹, and the bond energy is $(3.0)10^{-12}$ erg. These numbers and the corresponding $Y = 0.20$ are now used to calculate $1/J$. It is seen in Figure VI that the slope of the $1/J$ versus temperature curve agrees very well with the linewidth versus temperature data for K_2CuF_4 .

The compounds $(C_nH_{2n+1}NH_3)_2Cu$, $MnCl_4$ probably also have a temperature dependent J , which also contributes to the linear temperature dependence of the linewidth. $1/J$ was calculated with $Y = 0.02$, obtained from the previous tables, for the $CuCl_4$ dimer. The results are indicated in Figure VI. The calculated slope is about half the experimental slope, which indicates that spin diffusion and anti-symmetric exchange also contribute to the linear temperature dependence of the linewidth.

It is also necessary to explain the negligible temperature dependence of the linewidth for certain transition metal salts. The antiferromagnetic salt, $CuF_2 \cdot 2H_2O$ will be considered as an example. This compound has been extensively investigated by

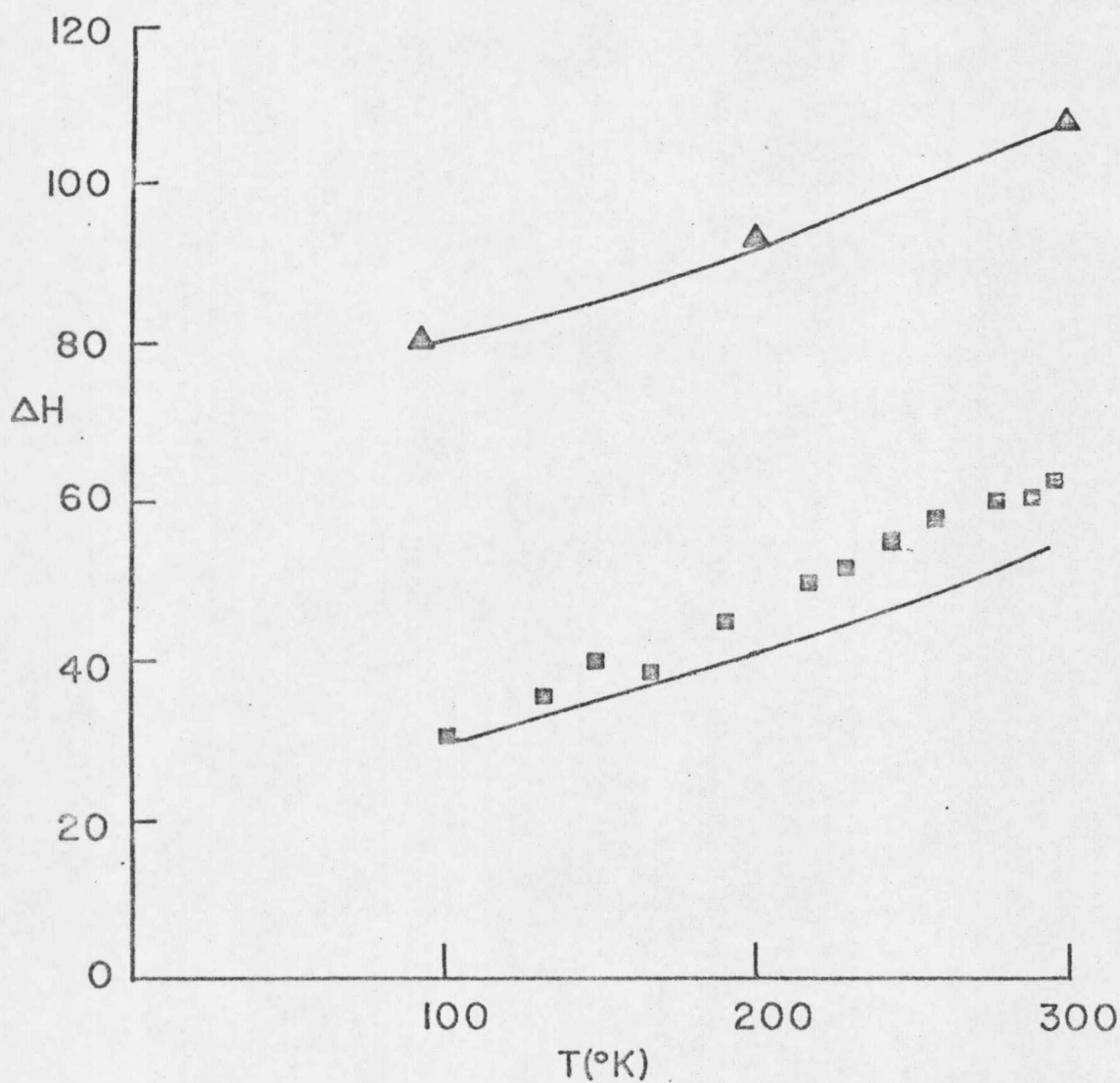
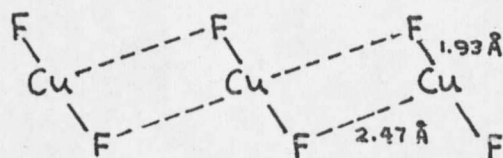


Figure VI

EPR linewidth versus temperature for K_2CuF_4 and $(nPr-NH_3)_2CuCl_4$. The triangles and squares are for K_2CuF_4 and $(nPr-NH_3)_2CuCl_4$ respectively, and the solid lines are the calculated linewidths for the appropriate values of the parameter Y .

Nagata and Date⁴⁵ above the Neel temperature, and they have shown that the linewidth stays approximately constant at temperatures above $3T_N$. From these results it appears as if $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ must be strongly bonded, or in other words Y should be small. The tables of the previous chapter are used to calculate Y for this compound; however, first it is necessary to consider the magnetic properties of the structure. Geller and Bond⁴⁶ have shown that the magnetic coupling occurs in CuF_2 chains as indicated below,



with each Cu and F strongly bonded to an extraplanar oxygen atom. It may seem as if the magnetic structure consists of weakly bonded CuF_2 molecules, which would probably have a large Y . However, each F atom is strongly bonded to another $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ group and the vibrational frequency is not determined by the weak Cu-F bond. Assuming that the modulation frequency is determined by the short Cu-F bond, the parameter Y is .03 for the reduced mass of the Cu-F-Cu molecule. From Figure V it can be seen that this value of Y does not result in appreciable temperature dependence, which is in agreement with experimental data.

VII. CONCLUSION

The exchange energy between two bound complexes has considerable temperature dependence for the appropriate choice of bond strengths and overlap parameters. Two assumptions were made in the process of developing this model: First, the Born-Oppenheimer approximation was assumed to be valid. Second, the model was applicable to a ML_4 dimer. Next we will investigate possible modifications in the theory if these assumptions are not made.

The Born-Oppenheimer approximation is certainly valid for transition metal salts because the crystal field splitting is much greater than the optical phonon energy. However, for rare earths the crystal field splitting and optical phonon energy are the same order of magnitude, so the Born-Oppenheimer approximation is no longer valid. In this case, there will be radiationless transitions to excited molecular orbitals, which will alter the exchange integral. J is temperature dependent in this case because of the electron-phonon interaction.

Another interesting case arises when we consider the exchange integral in a periodic lattice instead of a dimer. The one-electron state is now

$$\psi_i(r) = \exp(ik \cdot r) u_i(k, r)$$

where $u_i(k, r)$ is a Bloch function. If the center of the coordinate system is a lattice site, the variable r can be expressed as

$$r = R_n + r'$$

R_n can now be expanded in terms of phonon operators, which results in a temperature dependent exchange integral.

It may also be possible to explain other anomalous magnetic data with temperature dependent exchange. In particular, Reed et al. have recently shown that the specific heat of $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ has a term linear in temperature. This is unexplained but a temperature dependent J may be a simple explanation.

APPENDIX I

The harmonic oscillator states are calculated with

$$H' = V_3 (\delta R)^3$$

as a perturbation. In terms of vibron creation and destruction operators,

$$\delta R = i \sqrt{\frac{\hbar}{2m\omega}} (a^\dagger - a)$$

the perturbation is

$$H' = -i V_3 \left(\frac{\hbar}{2m\omega} \right)^{3/2} (a^\dagger a^\dagger a^\dagger - a^\dagger a a^\dagger - a^\dagger a^\dagger a + a^\dagger a a \\ - a a^\dagger a^\dagger + a a a^\dagger + a a^\dagger a - a a a).$$

Starting with the zeroth order state, $|n\rangle$, the first and second order corrections to $|n\rangle$ are now calculated. The first order correction is

$$|\psi_n^1\rangle = -i V_3 \left(\frac{\hbar}{2m\omega} \right)^{3/2} \left\{ \frac{\sqrt{(n+1)(n+2)(n+3)}}{E_n^0 - E_{n+3}^0} |n+3\rangle \right. \\ - \frac{(n+1)^{3/2}}{E_n^0 - E_{n+1}^0} |n+1\rangle - \frac{n \sqrt{n+1}}{E_n^0 - E_{n+1}^0} |n+1\rangle + \frac{(n-1)\sqrt{n}}{E_n^0 - E_{n-1}^0} |n-1\rangle \\ - \frac{(n+2)\sqrt{n+1}}{E_n^0 - E_{n+1}^0} |n+1\rangle + \frac{(n+1)\sqrt{n}}{E_n^0 - E_{n-1}^0} |n-1\rangle + \frac{n^{3/2}}{E_n^0 - E_{n-1}^0} |n-1\rangle \\ \left. - \frac{\sqrt{n(n-1)(n-2)}}{E_n^0 - E_{n-3}^0} |n-3\rangle \right\}$$

and the second order correction is

$$\begin{aligned}
|\psi_n^2\rangle = & -\left(\frac{\hbar}{2m\omega}\right)^3 V_3^3 \left\{ \frac{\sqrt{(n+1)\cdots(n+6)}}{(E_n^0 - E_{n+6}^0)(E_n^0 - E_{n+3}^0)} |n+6\rangle \right. \\
& - \frac{(n+2)^{3/2} (n+1)^{3/2}}{(E_n^0 - E_{n+2}^0)(E_n^0 - E_{n+1}^0)} |n+2\rangle - \frac{n(n+1) \sqrt{(n+1)(n+2)}}{(E_n^0 - E_{n+2}^0)(E_n^0 - E_{n+1}^0)} |n+2\rangle \\
& + \frac{(n-1)(n-2) \sqrt{n(n-1)}}{(E_n^0 - E_{n-2}^0)(E_n^0 - E_{n-1}^0)} |n-2\rangle - \frac{(n+2)(n+3) \sqrt{(n+1)(n+2)}}{(E_n^0 - E_{n+2}^0)(E_n^0 - E_{n+1}^0)} |n+2\rangle \\
& + \frac{n(n+1) \sqrt{n(n-1)}}{(E_n^0 - E_{n-2}^0)(E_n^0 - E_{n-1}^0)} |n-2\rangle + \frac{(n-1)^{3/2} n^{3/2}}{(E_n^0 - E_{n-2}^0)(E_n^0 - E_{n-1}^0)} |n-2\rangle \\
& \left. - \frac{\sqrt{n\cdots(n-5)}}{(E_n^0 - E_{n-6}^0)(E_n^0 - E_{n-3}^0)} |n-6\rangle \right\}
\end{aligned}$$

where ω is defined by $\hbar\omega = E_{n+1}^0 - E_n^0$.

The anharmonic oscillator state is now

$$|n\rangle = |n\rangle + |\psi_n^1\rangle + |\psi_n^2\rangle.$$

Now the matrix element I_n is calculated:

$$I_n = \langle n | J(\delta R) | n \rangle + \langle \psi'_n | J(\delta R) | \psi'_n \rangle + \langle \psi_n^2 | J(\delta R) | \psi_n^2 \rangle \\ + 2 \langle n | J(\delta R) | \psi'_n \rangle + 2 \langle n | J(\delta R) | \psi_n^2 \rangle + 2 \langle \psi'_n | J(\delta R) | \psi_n^2 \rangle.$$

Since I_n must be real, the following terms are zero:

$$\langle n | J(\delta R) | \psi'_n \rangle, \quad \langle \psi'_n | J(\delta R) | \psi_n^2 \rangle.$$

Each of the other four expressions are evaluated separately in terms of harmonic oscillator states, $|n\rangle$. $\langle n | J(\delta R) | n \rangle$ is already in the desired form; the other three are:

$$\langle n | J(\delta R) | \psi_n^2 \rangle = \left(\frac{\hbar}{2m\omega} \right)^3 V_3^2 \left\{ - \frac{\sqrt{(n+1)\dots(n+6)}}{(E_n^0 - E_{n+6}^0)(E_n^0 - E_{n+3}^0)} \right. \\ \times \langle n | J(\delta R) | n+6 \rangle + \frac{\sqrt{(n+1)(n+2)} (2(n+1)^2 + (n+2)(n+3))}{(E_n^0 - E_{n+2}^0)(E_n^0 - E_{n+1}^0)} \langle n | J(\delta R) | n+2 \rangle \\ - \frac{\sqrt{n(n-1)} ((n-1)(n-2) + 2n^2)}{(E_n^0 - E_{n-2}^0)(E_n^0 - E_{n-1}^0)} \langle n | J(\delta R) | n-2 \rangle \\ \left. + \frac{\sqrt{(n-5)\dots n}}{(E_n^0 - E_{n-6}^0)(E_n^0 - E_{n-3}^0)} \langle n | J(\delta R) | n-6 \rangle \right\},$$

Next it is necessary to evaluate matrix elements of the form

$$\langle k | J(\delta R) | l \rangle,$$

which is equivalent to the following integral

$$I_{nn} = \frac{J_0}{2^n n!} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left(-v^2 - \frac{\lambda}{a} v\right) H_n(v) H_n(v) dv$$

for the diagonal matrix element (here $a = \sqrt{\frac{m\omega}{\hbar}}$).

This can be evaluated:

$$I_{nn} = J_0 e^{\frac{\lambda^2}{4a^2}} L_n^0\left(-\frac{\lambda^2}{2a^2}\right),$$

and the off diagonal matrix elements are:

$$I_{kl} = \frac{J_0}{2^{\frac{k+l}{2}} \sqrt{k!l!}} e^{\frac{\lambda^2}{4a^2}} 2^l k! \left(-\frac{\lambda}{2a}\right)^{l-k} L_1^{l-k}\left(-\frac{\lambda^2}{2a^2}\right)$$

for $l > k$. L_1^{l-k} is an associated Laguerre polynomial with a negative argument. The necessary matrix elements are:

$$\langle n | J(\delta R) | n \rangle = J_0 e^{\gamma/2} L_n^0(-\gamma)$$

$$\langle n+1 | J(\delta R) | n+3 \rangle = 2 J_0 \gamma e^{\gamma/2} \frac{L_{n+3}^2(-\gamma)}{\sqrt{(n+2)(n+3)}}$$

$$\begin{aligned}
\langle \psi'_n | J(\delta R) | \psi'_n \rangle &= \left(\frac{\hbar}{2m\omega} \right)^3 V_3^2 \left\{ \frac{(n+1)(n+2)(n+3)}{(E_n^0 - E_{n+3}^0)^2} \langle n+3 | J(\delta R) | n+3 \rangle \right. \\
&+ \frac{((n+1)^{3/2} + n(n+1)^{1/2} + (n+2)(n+1)^{1/2})^2}{(E_n^0 - E_{n+1}^0)^2} \langle n+1 | J(\delta R) | n+1 \rangle \\
&+ \frac{(n^{3/2} + (n+1)n^{1/2} + (n-1)n^{1/2})^2}{(E_n^0 - E_{n-1}^0)^2} \langle n-1 | J(\delta R) | n-1 \rangle \\
&+ \frac{n(n-1)(n-2)}{(E_n^0 - E_{n-3}^0)^2} \langle n-3 | J(\delta R) | n-3 \rangle \\
&- 2 \frac{(n+1)^{3/2} \sqrt{(n+1)(n+2)(n+3)}}{(E_n^0 - E_{n+3}^0)(E_n^0 - E_{n+1}^0)} \langle n+1 | J(\delta R) | n+3 \rangle \\
&+ 2 \frac{\sqrt{(n+1)(n+2)(n+3)} (n^{3/2} + n^{1/2}(n+1) + n^{1/2}(n-1))}{(E_n^0 - E_{n+3}^0)(E_n^0 - E_{n-1}^0)} \langle n-1 | J(\delta R) | n+3 \rangle \\
&- 2 \frac{\sqrt{(n-2)(n-1) \cdots (n+3)}}{(E_n^0 - E_{n+3}^0)(E_n^0 - E_{n-3}^0)} \langle n-3 | J(\delta R) | n+3 \rangle \\
&- 2 \frac{(3n+3)\sqrt{n+1} + 3n\sqrt{n}}{(E_n^0 - E_{n+1}^0)(E_n^0 - E_{n-1}^0)} \langle n-1 | J(\delta R) | n+1 \rangle
\end{aligned}$$

$$+ 2 \frac{(3n+3) \sqrt{(n+1)n \dots (n-2)}}{(E_n^0 - E_{n+1}^0)(E_n^0 - E_{n-3}^0)} \langle n+1 | J(\delta R) | n-3 \rangle$$

$$- 2 \frac{3n^2 \sqrt{(n-1)(n-2)}}{(E_n^0 - E_{n-1}^0)(E_n^0 - E_{n-3}^0)} \langle n-1 | J(\delta R) | n-3 \rangle ,$$

$$\langle n-1 | J(\delta R) | n+3 \rangle = 4J_0 Y^2 e^{Y/2} \frac{1}{\sqrt{n \cdots (n+3)}} L_{n+3}^4(-Y)$$

$$\langle n-3 | J(\delta R) | n+3 \rangle = 8J_0 Y^3 e^{Y/2} \frac{1}{\sqrt{(n-2) \cdots (n+3)}} L_{n+3}^6(-Y)$$

$$\langle n-1 | J(\delta R) | n+1 \rangle = 2J_0 Y e^{Y/2} \frac{1}{\sqrt{n(n+1)}} L_{n+1}^2(-Y)$$

$$\langle n-3 | J(\delta R) | n+1 \rangle = 4J_0 Y^2 e^{Y/2} \frac{1}{\sqrt{(n-2) \cdots (n+1)}} L_{n+1}^4(-Y)$$

$$\langle n-3 | J(\delta R) | n-1 \rangle = 2J_0 Y e^{Y/2} \frac{1}{\sqrt{(n-2)(n-1)}} L_{n-1}^2(-Y)$$

$$\langle n | J(\delta R) | n+6 \rangle = 8J_0 Y^3 e^{Y/2} \frac{1}{\sqrt{(n+1) \cdots (n+6)}} L_{n+6}^6(-Y)$$

$$\langle n | J(\delta R) | n+2 \rangle = 2J_0 Y e^{Y/2} \frac{1}{\sqrt{(n+1)(n+2)}} L_{n+2}^2(-Y)$$

$$\langle n | J(\delta R) | n-2 \rangle = 2J_0 Y e^{Y/2} \frac{1}{\sqrt{n(n-1)}} L_n^2(-Y)$$

$$\langle n | J(\delta R) | n-6 \rangle = 8J_0 Y^3 e^{Y/2} \frac{1}{\sqrt{(n-5) \cdots n}} L_n^6(-Y)$$

These integrals are now used in each term of the expression for I_n with the parameter Y used as the variable.

$$\begin{aligned}
\langle \psi_n' | J(\delta R) | \psi_n' \rangle = & J_0 \frac{Y}{4} e^{Y/2} \left\{ \frac{(n+1)(n+2)(n+3)}{9} L_{n+3}^0(-Y) \right. \\
& + 9(n+1)^3 L_{n+1}^0(-Y) + 9n^3 L_{n-1}^0(-Y) + \frac{n(n-1)(n-2)}{9} L_{n-3}^0(-Y) \Big\} \\
& + J_0 \frac{Y}{2} e^{Y/2} \left\{ -(n+1)^2 Y L_{n+3}^2(-Y) - n Y^2 L_{n+3}^4(-Y) \right. \\
& + \frac{1}{9} Y^3 L_{n+3}^6(-Y) + 3(2n+1) Y L_{n+1}^2(-Y) \\
& \left. - (n+1) Y^2 L_{n+1}^4(-Y) - n Y L_{n-1}^2(-Y) \right\} , \\
\langle n | J(\delta R) | \psi_n^2 \rangle = & J_0 \frac{Y}{16} e^{Y/2} \left\{ -\frac{1}{18} Y^3 L_{n+6}^6(-Y) \right. \\
& + \frac{1}{2} (2(n+1)^2 + (n+2)(n+3)) Y L_{n+2}^2(-Y) \\
& \left. - \frac{1}{2} (2n^2 + (n-2)(n-1)) Y L_n^2(-Y) + \frac{1}{18} Y^3 L_n^6(-Y) \right\} .
\end{aligned}$$

APPENDIX II

PROGRAM TO CALCULATE THE THERMAL AVERAGE OF I

```

    LET Y=.02
    FOR T=1 TO 301 STEP 50
    LET J0=0
    LET F1=0
    LET K=0
    FOR A=0 TO 20 STEP 1
    GO TO 226
40  LET A1=0
    FOR M=0 TO N STEP 1
    LET R=1
    FOR X=T TO N+K STEP 1
    LET R=X*R
    NEXT X
    LET F=1
    FOR X=1 TO M+K STEP 1
    LET F=F*X
    NEXT X
    LET U=1
    FOR X=1 TO M STEP 1
    LET U=U*X
    NEXT X
    LET A1=A1+R/(S*F*U)*Y
    NEXT M
    RETURN
226 LET N=A+3
    GO SUB 40
    LET B1=(A+1)*(A+2)*(A+3)/9*A1
    LET N=A+1
    GO SUB 40
    LET B2=9*(A+1)+3*A1
    LET N=A
    GO SUB 40
    LET B5=A1
    IF(A-1)<0 THEN 380
    LET N=A-1
    GO SUB 40
    LET B3=9*A+3*A1
    IF(A-3)<0 THEN 380
    LET N=A-3
    GO SUB 40
    LET B4=A*(A-1)*(A-2)/9*A1

```

```

380 LET B=B1+B2+B3+B4
  LET N=A+3
  LET K=2
  GO SUB 40
  LET C1=-(A+1)*2*Y*A1
  LET N=A+3
  LET K=4
  GO SUB 40
  LET C2=-A*Y*2*A1
  LET N=A+3
  LET K=6
  GO SUB 40
  LET C3=Y*3/9*A1
  LET N=A+1
  LET K=2
  GO SUB 40
  LET C4=3*(2*A+1)*Y*A1
  LET N=A+1
  LET K=4
  GO SUB 40
  LET C5=-(A+1)*Y*2*A1
  IF(A-1)<0 THEN 710
  LET N=A-1
  LET K=2
  GO SUB 40
  LET C6=-A*Y*A1
710 LET C=C1+C2+C3+C4+C5+C6
  LET C=2*C
  LET N=A+6
  LET K=6
  GO SUB 40
  LET G1=-Y*3*A1/18
  LET N=A+2
  LET K=2
  GO SUB 40
  LET G2=(2*(A+1)*2+(A+2)*(A+3))*Y*A1/2
  IF(A-2)<0 THEN 797
  LET N=A
  LET K=2
  GO SUB 40
  LET G3=-(2*A*2+(A-1)*(A-2))*Y*A1/2
  IF(A-6)<0 THEN 797
  LET N=A
  LET K=6
  GO SUB 40

```

```
LET G4=Y*3*A1/I8
797 LET G=G1+G2+G3+G4
LET G=G/2
LET D=B+C+G
LET Z=4/(T*Y)
LET P=(1-EXP(-Z))*EXP(-Z*A)
LET J=Y/4*EXP(Y/2)*D
LET B6=B5*EXP(Y/2)
LET J1=P*J
LET E2=P*B6
LET J0=J0+J1
LET E1=E1+E2
NEXT A
LET E3=E1+J0
PRINT T;E3
PRINT
NEXT T
```

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