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SUM RULE FOR NUCLEAR QUADRUPOLE INTERACTION

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We derive a sum rule relating the electric field gradient at the nucleus to elastic dipole matrix elements. It appears to present a useful alternative to Sternheimer corrections.

While atomic hyperfine intervals may be measured with a precision attainable almost nowhere else in physics, the extraction of values for nuclear moments from hfs determinations is hampered by the absence of exact atomic wave functions. For example, in the case of the interaction of the nuclear electric quadrupole moment with the atomic electrons one needs to know the gradient of the electric field produced by the electrons at the position of the nucleus, proportional to the expectation value of the operator q , where

$$q = \sum_{i=1}^n \frac{1}{r_i^3} P_2(\cos\theta_i). \quad (1)$$

The normal state of affairs is that the best available approximate wave functions are of the central-field variety. The field gradient parameter $\langle 0|q|0 \rangle$ is evaluated from these, with only the valence electrons making a nonvanishing contribu-

tion. The result is improved by the Sternheimer¹⁻³ approximation, which corrects for the interactions between valence electrons and the quadrupole moment induced in the closed shells by the nonspherical nucleus. Solutions of inhomogeneous Schrödinger equations are required to determine the effect of this distortion. Since hyperfine measurements include all contributions to the quadrupole interaction, a direct experimental check of the shielding terms cannot be made. It would be useful to have other means for estimating $\langle 0|q|0 \rangle$.

Our purpose in writing this article is to point out an alternate method for determining the parameter $\langle 0|q|0 \rangle$. The nonrelativistic Hamiltonian H_0 for an n -electron atom, nuclear charge N , without hyperfine structure is given by

$$H_0 = \sum_{i=1}^n \frac{p_i^2}{2m} - Ne^2 \sum_{i=1}^n \frac{1}{r_i} + e^2 \sum_{i < j} \sum_{j=2}^n \frac{1}{r_{ij}}. \quad (2)$$

Consider the double commutator

$$[[H_0, \sum_{i=1}^n P_{zi}], \sum_{j=1}^n P_{zj}] = \hbar^2 Ne^2 \sum_{i=1}^n \sum_{j=1}^n \left[\frac{z_i}{r_i^3}, \frac{\partial}{\partial z_j} \right] = \hbar^2 Ne^2 \sum_{i=1}^n \left(\frac{\partial^2}{\partial z_i^2} \frac{1}{r_i} \right), \quad (3)$$

where P_{zi} is the z component of momentum for electron i . Since it is the Green's function for the Laplacian, some caution must be exercised in differentiating $1/r$ twice with respect to one of the rectangular coordinates, lest delta-function type singularities be omitted. To take account of this possibil-

ity, we express $\partial^2 f / \partial z^2$, where f is an arbitrary function of r , in terms of its Laplacian,

$$\frac{\partial^2 f}{\partial z^2} = \frac{1}{3} \nabla^2 f + \frac{2}{3} P_2(\cos\theta) \nabla^2 f - \frac{2}{r} P_2(\cos\theta) \frac{df}{dr},$$

so that

$$\hbar^2 N e^2 \sum_{i=1}^n \left(\frac{\partial^2}{\partial z_i^2} \frac{1}{r_i} \right) = \hbar^2 N e^2 \sum_{i=1}^n \left[-\frac{4\pi}{3} \delta(\vec{r}_i) - \frac{8\pi}{3} P_2(\cos\theta_i) \delta(\vec{r}_i) + 2P_2(\cos\theta_i) \frac{1}{r_i^3} \right].$$

All matrix elements of the operator

$$\sum_{i=1}^n P_2(\cos\theta_i) \delta(\vec{r}_i)$$

vanish. The delta function is expressible in terms of a double commutator

$$-4\pi \hbar^2 N e^2 \sum \delta(\vec{r}_i) = \left[[H_0, \sum_{i=1}^n \vec{P}_i], \cdot \sum_{j=1}^n \vec{P}_j \right]. \quad (4)$$

This yields the sum rule

$$2 \sum_k (\epsilon_k - \epsilon_0) |\langle 0 | \sum_{i=1}^n \vec{P}_i | k \rangle|^2 = 4\pi \hbar^2 N e^2 \langle 0 | \sum_{i=1}^n \delta(\vec{r}_i) | 0 \rangle. \quad (5)$$

The electric field gradient parameter then becomes

$$\langle 0 | q | 0 \rangle = \frac{1}{2\hbar^2 N e^2} \left\{ \langle 0 | \left[[H_0, \sum_{i=1}^n P_{zi}], \sum_{j=1}^n P_{zj} \right] | 0 \rangle - \frac{1}{3} \langle 0 | \left[[H_0, \sum_{i=1}^n \vec{P}_i], \cdot \sum_{j=1}^n \vec{P}_j \right] | 0 \rangle \right\}, \quad (6)$$

which is identical to the sum rule

$$\langle 0 | q | 0 \rangle = \frac{1}{2\hbar^2 N e^2} \sum_k (\epsilon_0 - \epsilon_k) \left\{ |\langle 0 | \sum_{i=1}^n P_{zi} | k \rangle|^2 - \frac{1}{3} |\langle 0 | \sum_{i=1}^n \vec{P}_i | k \rangle|^2 \right\}. \quad (7)$$

Since the matrix elements of the momentum operator govern electric dipole transition rates, $\langle 0 | q | 0 \rangle$ may in principle be deduced from measurements of radiative absorption and/or emission coefficients.

Neither sufficiently accurate nor abundant data are available to be of use in determining $\langle 0 | q | 0 \rangle$ from experimental oscillator strengths. The sum rule may be valuable in theoretical calculations of the parameter, however. If the approximate wave functions are of the Hartree-Fock or similar type, they satisfy a variational principle for the energy and one expects good values for the excitation energies appearing in Eq. (7). In addition the momentum form of the dipole matrix element usually gives, for Hartree-Fock wave functions, values substantially closer to experiment than either of the other forms.

To examine the utility of the sum rule for such calculations, we computed the ratio of $\langle 0 | q | 0 \rangle$ as deduced from Eq. (1) to that obtained from the sum rule for the ground state of boron, using the Hartree-Fock-Slater wave functions of Herman and Skillman.⁴ [Since we regard this as a test

and not a definitive calculation, we actually evaluated the expectation value of the double commutator of Eq. (6), using the Hartree-Fock-Slater Hamiltonian, in preference to explicitly performing the summations prescribed by Eq. (7). This is equivalent to using the sum rule with ground- and excited-state wave functions obtained from the same single-particle potential, rather than from separate self-consistent field calculations for each state.] Our result for the ratio is 1.156, which is to be compared with Sternheimer's 1.17 obtained with Hartree-Fock wave functions.⁵

To summarize, we have derived a sum rule for the parameter giving the value of the gradient of the electronic electric field at the position of the atomic nucleus, which, in principle, enables it to be derived from measurements of radiative transitions. It appears to be immediately useful in providing a new method for calculating $\langle 0 | q | 0 \rangle$.

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EXPERIMENTAL PROOF OF THE STRONG COUPLING
BETWEEN THE ELECTRON SPIN-SPIN RESERVOIR AND A NUCLEAR SPIN SYSTEM
IN DILUTE PARAMAGNETIC CRYSTALS

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Experiments are described in which the nuclear Zeeman temperature T_n and the temperature of the electron dipole-dipole interaction system T_{int} in a dilute paramagnetic crystal are measured simultaneously. The spin-lattice relaxation times of these two systems turn out to be equal, thus yielding a direct evidence of the strong coupling between these systems.

The concept of spin temperature in a rotating frame as introduced by Redfield¹ has led to a better understanding of the behavior of spin systems in solids subjected to strong rf fields. Redfield's theory, which was only valid in the limit of strong rf saturation, was extended by Provotorov² to rf fields of arbitrary intensity. He showed that in strong static magnetic fields two distinct temperatures should be assigned to the spin system: one temperature T_e for the Zeeman system and a temperature T_{int} to describe the dipole-dipole interaction system. He also derived equations for the time dependence of both temperatures under the influence of an rf field and of spin-lattice relaxation. Further calculations of the shape of the resonance absorption signal when Provotorov's concept of an interaction temperature T_{int} was taken into account were carried out by Rodak.³ Atsarkin and Morshnev⁴ performed line-shape experiments which confirmed the existence of a temperature T_{int} different from T_e . They were able to observe the time dependence of T_e and T_{int} by studying the shape of a paramagnetic resonance line which had been saturated by a slightly detuned microwave field.

An extension of these ideas to explain the results of nuclear dynamic polarization and nuclear relaxation experiments in dilute paramagnetic crystals provided further evidence for the existence of an interaction system of the paramagnetic ions. Actually measurements of the proton spin-lattice relaxation times in such crystals led to the idea that the nuclear Zeeman system could be strongly coupled to the interaction system of the paramagnetic ions.⁵ Nuclear-dynamic-polarization experiments were carried out in order to

confirm these views.⁶ In performing these experiments however, only the nuclear resonance signal, which is inversely proportional to the nuclear Zeeman temperature T_n , was monitored. Thus only indirect information about the behavior of the interaction system was obtained.

In the experiments to be discussed below the nuclear Zeeman temperature T_n as well as the interaction temperature T_{int} were measured simultaneously in order to prove that T_n and T_{int} had the same time behavior, with a relaxation time equal to the nuclear spin-lattice relaxation time. This would be a direct proof of the strong coupling of the nuclear spins to the electron-spin interaction system.

The experiments were performed at 1.5 K in a single crystal of $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 0.24\text{H}_2\text{O}$ containing 2% Nd. The magnetic field H_0 of about 2.5 kG was directed perpendicular to the c axis. The paramagnetic resonance line of the Nd ions was observed at 9000 MHz, the proton resonance of the crystal waters occurred at about 10 MHz.

The intensity of the proton resonance signal was used as a measure of the nuclear spin temperature T_n . The interaction temperature T_{int} was derived from the shape of the Nd resonance line. According to Provotorov¹ the rf absorption $\mathcal{G}(\Delta, t)$ of a spin system is given by

$$\mathcal{G}(\Delta, t) = P(\Delta) \left[\frac{\nu_e}{T_e(t)} + \frac{\Delta}{T_{\text{int}}(t)} \right], \quad (1)$$

where $P(\Delta)$ is the transition probability due to the rf field and includes the usual line-shape function. ν_e is the Larmor frequency of the electron-spins. $\nu_e + \Delta$ is the frequency of the applied rf