cies $\omega_\kappa$ which might culminate in additional solutions within the band in some cases and (b) new solutions outside the band.

The choice of the center-of-mass coordinates $x_0^i$ for the "lattice" is not the only possibility; we could have chosen, as well, any three coordinates of the molecule to which a single effective mass can be attached. In the case of interstitial masses, for instance, one may keep the old lattice coordinates, taking the interstitials as the molecular system ($\xi_\nu^i$).

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# Vibrational Corrections to Nuclear Magnetic Resonance Second Moments*

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The effect of rapid nuclear motions on the observable second moments of nuclear-magnetic resonance-absorption lines is considered by the method of lattice harmonics. An explicit formula is given in terms of time-averaged values of lattice harmonics. In the case of lattice vibrations in a cubic solid with a cubic point group at the nuclear site, the observable correction to the rigid lattice second moment is zero up to and including the second order in the relative nuclear amplitudes of vibration. In general, only the anisotropic vibrations contribute in second order to the observable second moment.

THE effects of nuclear motion on nuclear-magnetic resonance lines of nuclei in crystals are well recognized and generally referred to as "motional narrowing" since the nuclear motion produces a reduction in the observed resonance linewidth and moments. Denoting the truncated dipolar interaction Hamiltonian of Van Vleck[1] by $\mathcal{H}$ and the total nuclear spin by $\mathbf{I}$, the second moment is proportional to the trace of $\langle[\mathcal{H},I_x]^2\rangle$, where the angular bracket indicates the time average of the enclosed quantity. In the presence of nuclear motion which causes a time dependence of $\mathcal{H}$ and which is rapid compared to the Larmor precession of the nuclei in the external magnetic field, $\langle[\mathcal{H},I_x]^2\rangle$ may be rewritten as follows:

$$\langle[\mathcal{H},I_x]^2\rangle=[\langle\mathcal{H}\rangle,I_x]^2+\langle[\mathcal{H}-\langle\mathcal{H}\rangle,I_x]^2\rangle. \quad (1)$$

Equation (1) results since $\mathcal{H}=\langle\mathcal{H}\rangle+(\mathcal{H}-\langle\mathcal{H}\rangle)$ and $\langle[\langle\mathcal{H}\rangle,I_x][\mathcal{H}-\langle\mathcal{H}\rangle,I_x]\rangle=0$. As pointed out by several authors,[2] the second term in (1) gives a contribution to the second moment in the far wings of the absorption line which is not observed in a conventional magnetic resonance experiment. In the following, we will refer to the second moment computed by taking the trace of $\langle[\mathcal{H},I_x]^2\rangle$ and $[\langle\mathcal{H}\rangle,I_x]^2$ as $M_2'$ and $M_2^{\rm obs}$, respectively. The experimentally measured second moment will correspond to $M_2^{\rm obs}$. $M_2^{\rm obs}$ has also been referred to as the "observable" part of the second moment.[2]

An alternative, but equivalent way of viewing the situation is to note that if a nuclear spin undergoes a periodic motion during which it experiences a range of local magnetic fields due to neighboring nuclei, and, further, if the period of this motion is very short compared to the period of Larmor precession, then the magnetic moment will respond only to the mean local field. Thus, in computing the mean square local field, the local field must first be time averaged corresponding to the first term of Eq. (1). The fourth moment is proportional to $\langle[\mathcal{H},[\mathcal{H},I_x]]^2\rangle$ which may be seen from arguments similar to those given above yields an observable part which is proportional to $[\langle\mathcal{H}\rangle,[\langle\mathcal{H}\rangle,I_x]]^2$ when the motion is fast.

For a rigid lattice, the dependence of the second moment on the orientation of the crystal under study may be conveniently expressed in terms of the lattice harmonics of the point group of the crystal[3] as follows (for only one magnetic nucleus per unit cell):

$$M_2=12\pi\gamma^4\hbar^2I(I+1)\times\sum_k\sum_{L\alpha}\frac{[C(22L;00)]^2}{2L+1}\frac{X_L{}^{1\alpha*}(jk)}{r_{jk}{}^6}X_L{}^{1\alpha}(\theta,\phi), \quad (2)$$

where $L$ takes on the values 0, 2, and 4, $C(22L;00)$ is a Clebsch-Gordan coefficient, $X_L{}^{1\alpha}$ denotes a lattice harmonic of order $L$ belonging to the identity representation of the crystal point group, $jk$ and $(\theta,\varphi)$ denote the respective orientations of the radius vector $\mathbf{r}_{jk}$ and the external magnetic field relative to the crystal coordinate system.

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[1] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[2] See, for example, the review by A. Abragam, in *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. 10.

[3] D. E. O'Reilly and T. Tsang, Phys. Rev. **128**, 2639 (1962).

To discuss the effects of nuclear motion on $M_2$, we note that[1] $[\mathcal{H},I_x]$ is proportional to

$$b_{jk}=-3(4\pi/5)^{1/2}\gamma^2\hbar^2Y_{20}(\vec{jk}),$$

where $\vec{jk}$ refers to the orientation of the radius vector $\mathbf{r}_{jk}$ relative to the laboratory coordinate system whose $z$ axis coincides with the direction of the external field. Hence,

$$M_2^{\text{obs}}=[I(I+1)/3\hbar^2]\textstyle\sum_k\langle b_{jk}\rangle^2 \text{ rad}^2 \text{ sec}^{-2}. \quad (3)$$

Transforming from laboratory to crystal coordinate system and then from spherical to lattice harmonics,[3] $b_{jk}$ may be written as

$$b_{jk}=-(12\pi/5)\gamma^2\hbar^2r_{jk}^{-3}\textstyle\sum_{\mu\alpha i}X_2^{\mu\alpha i*}(jk)X_2^{\mu\alpha i}(\theta,\varphi). \quad (4)$$

The time average of (5) is

$$\langle b_{jk}\rangle=-(12\pi/5)\gamma^2\hbar^2 \times\textstyle\sum_{\mu\alpha i}\langle X_2^{\mu\alpha i*}(jk)r_{jk}^{-3}\rangle X_2^{\mu\alpha i}(\theta,\phi). \quad (5)$$

Hence,

$$M_2^{\text{obs}}=(48\pi^2/25)\gamma^4\hbar^2I(I+1) \times\textstyle\sum_{k,\mu,\alpha,i,\mu',\alpha',i'}\langle r_{jk}^{-3}X_2^{\mu\alpha i*}(jk)\rangle \times\langle r_{jk}^{-3}X_2^{\mu'\alpha'i'}(jk)\rangle X_2^{\mu\alpha i}(\theta,\phi)X_2^{\mu'\alpha'i'*}(\theta,\phi). \quad (6)$$

As we have shown previously,[3] the group property of the rotation operators for crystals may be used to prove that only those terms with $\mu=\mu'$ and $i=i'$ do not vanish in (6). Furthermore, it has been also shown previously[3] that $\sum_k X_2^{\mu\alpha i*}(jk)X_2^{\mu\alpha' i}(jk)$ is independent of $i$. Using the lattice harmonics coupling coefficients as defined in Ref. 3, Eq. (6) may be written as

$$M_2^{\text{obs}}=(48\pi^2/25)\gamma^4\hbar^2I(I+1)\sum_{L=0,2,4}\sum_{A,k,\mu,\alpha,\alpha'} \times[\textstyle\sum_i\langle r_{jk}^{-3}X_2^{\mu\alpha i*}(jk)\rangle\langle r_{jk}^{-3}X_2^{\mu\alpha' i}(jk)\rangle] \times d_\mu^{-1}\langle 2(\mu\alpha),2(\mu\alpha')\,|\,LA\rangle X_L^{1A}(\theta,\phi), \quad (7)$$

where $d_\mu$ is the dimensionality of the $\mu$th representation.

For a rigid lattice, the angular brackets in (7) may be omitted. We can easily show that

$$\frac{25}{(2L+1)4\pi}[C(22L;00)]^2X_L^{1A}(jk) =\textstyle\sum_{\mu\alpha\alpha'}d_\mu^{-1}\langle 2(\mu\alpha),2(\mu\alpha')\,|\,LA\rangle \times[\sum_i X_2^{\mu\alpha i*}(jk)X_2^{\mu\alpha i}(jk)].$$

From this, (2) follows directly from (7).

Now we will consider the effect of lattice vibrations. The time-average value of quantities in (7) may be computed by expansion in a Taylor's series about the equilibrium positions. Denoting $X_2^{\mu\alpha i}(jk)r_{jk}^{-3}$ by $\phi$, then one obtains up to and including second-order terms:

$$\langle\phi\rangle=\phi_0+\sum_i\left(\frac{\partial\phi}{\partial x_i}\right)\langle\Delta x_i\rangle+\tfrac{1}{2}\sum_{ij}\left(\frac{\partial^2\phi}{\partial x_i\partial x_j}\right)_0\langle\Delta x_i\Delta x_j\rangle. \quad (8)$$

The subscript 0 refers to the equilibrium positions. By definition, $\langle\Delta x_i\rangle=0$.

Let us first consider the case of cubic point group symmetry at a nuclear site. Then we have $\langle\Delta x_i\Delta x_j\rangle=\delta_{ij}\Delta^2$, where $\Delta^2$ is the relative mean-square amplitude of vibration of the nuclei. It is also true that $\nabla^2\phi=0$ since $\nabla^2(r^{-3}Y_{2m}(\theta,\phi))=0$ for any $m$ and $X_2^{\mu\alpha i}$ is a linear combination of second-order spherical harmonics. Hence, up to and including second order in the relative nuclear displacements, the observable correction to the rigid lattice second moment due to lattice vibrations is zero. (In Ref. 3,[4] we have calculated the quantity $M_2'$ for $F^{19}$ in $CaF_2$ and for $Al^{27}$ in Al. This calculated vibration correction, however, is unobservable.[2]) The disagreement between the calculated second moments based on rigid lattice and the experimental value is hardly significant for $CaF_2$. For aluminum metal, the difference is as large as 20%, and is probably associated with quadrupolar interactions of the nuclei with electric field gradients produced by defects in the metal.

For symmetries other than cubic, the above arguments are still valid in the case of isotropic vibrations. That is, the observed second moments are not affected by isotropic nuclear vibrations. However, anisotropic vibrations may contribute to the observed second moments.

[4] See Secs. VIA, VIB, and Appendix B of Ref. 3.