DFT Studies of Temperature Effects in Nuclear Quadrupole Resonance

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Outline

1. NQR in the static lattice
   - The quadrupole interaction
   - The electric field gradient and the quadrupole copuling constant
   - NQR transition frequencies
2. T-dependence of NQR frequencies
   - The Bayer-Kushida (BK) model
3. Failures of the model
   - Volume dependence of NQR
   - Density functional theory for volume correction and molecular dynamics

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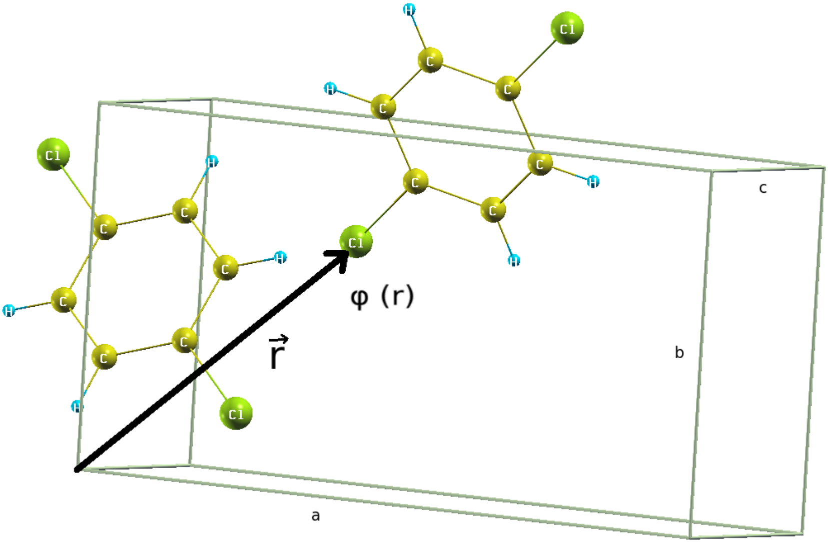

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The electric field gradient

- The nuclear quadrupole moment of a nucleus $Q_{ij} = Q$ ineracts with the gradient of the electric field gradient produced by the surrouding charges

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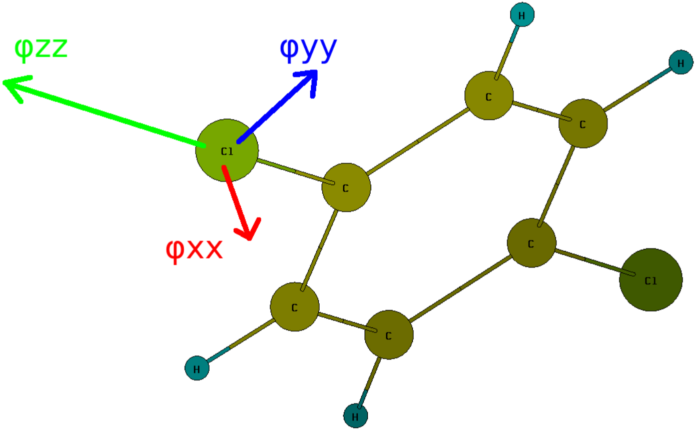
- X, Y, Z are the principal axes of the EFG at the nucleus.

NQR in the static lattice

EFG at nuclear site



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η: asymmetry parameter

$$\eta = \frac{\phi_{yy} - \phi_{xx}}{\phi_{zz}} = \frac{\frac{\partial^2 \phi}{\partial y^2} - \frac{\partial^2 \phi}{\partial x^2}}{\frac{\partial^2 \phi}{\partial z^2}} \tag{1}$$

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Pure quadrupole transition frequendcies

- NQR frequencies are proportional to the principal EFG component $q = \frac{\phi_{zz}}{e}$ times a factor involving η.

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- NQR frequencies are proportional to the principal EFG component $q = \frac{\phi_{zz}}{e}$ times a factor involving η.
- The NQR transition frequencies also depend on the isotope spin. Typical nuclei are ^{35}Cl having spin $\frac{3}{2}$ and ^{14}N with spin 1

NQR in the static lattice

Pure quadrupole transition frequendcies

NQR transition frequency for nuclear spin $I = \frac{3}{2}$

There is only one transition in this case

$$\nu = \frac{1}{2}\frac{e^2qQ}{\hbar}\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}} = \frac{1}{2}C_q\left(1+\frac{\eta^2}{3}\right)^{\frac{1}{2}}$$

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NQR transition frequencies for nuclear spin $I = 1$

If η is not zero, there are three transitions.

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- recalling:

$$C_q = \frac{e^2 qQ}{\hbar} = \frac{e\phi_{zz}}{\hbar}; \qquad \eta = \frac{\phi_{yy} - \phi_{xx}}{\phi_{zz}}$$

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- NQR prediction $<=>$ knowldge of a precise crystal structure and $\phi(\vec{r})$ everywhere in it.
- Description of NQR T-dependence requires consideration of internal motions in the lattice.
- Therefore the model described cannot address T-dependence.

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affects of internal motions

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- NQR frequencies have a sharp T-dependence
- The static lattice theory discussed does not and cannot address the T-dependence
- The T-dependence is a result of internal motions in the solid

T-dependence of NQR frequencies

Horst Bayer was the first to address NQR T-dependence in 1951

Zeitschrift für Physik, Bd. 130, S. 227—238 (1951).

Zur Theorie der Spin-Gitterrelaxation in Molekülkristallen*.

Von

HORST BAYER, Göttingen.

Mit 5 Figuren im Text.

(Eingegangen am 17. Mai 1951.)

Die vorliegende Arbeit soll einen Beitrag zur Theorie der Spin-Gitterrelaxation in Molekülkristallen mit Quadrupolkopplung liefern. Es wird versucht, die Meßergebnisse von DEHMELT und KRÜGER[1,2] am Dichloräthylen (CHCl = CHCl) theoretisch zu deuten. Die schwache Temperaturabhängigkeit der Kernquadrupolresonanzfrequenz kann erklärt werden, wenn man die Moleküle im Gitterverband als quantenmechanische harmonische Oszillatoren auffaßt, die Torsionsschwingungen ausführen und deren Amplitude temperaturabhängig ist. Dabei ist zu bedenken, daß der Quadrupolkern über den elektrischen Feldgradienten der homöopolaren Bindungselektronen energetisch mit dem übrigen Molekül gekoppelt ist.

T-dependence of NQR frequencies

Lattice vibrations: the Bayer-Kushida (BK) model

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- Show image from Das, Hahn

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- However a quadrupole undergoing motion will experience an effective EFG resulting from the average EFG smeared over its oscillatory motion
- The effective EFG experienced by the nucleus in motion is smaller in magnitude than that of the static lattice

- Consider small rotations θ_x, θ_y, θ_z sendint the coordinates to the primed system

T-dependence of NQR frequencies

Lattice vibrations: the Bayer-Kushida (BK) model

- Consider small rotations θ_x, θ_y, θ_z sendint the coordinates to the primed system
- Want to relate the efgs in the two coordinate systems, e.g. relate ϕ_{ij} to $\phi_{i'j'} = \phi'_{ij}$

T-dependence of NQR frequencies

Lattice vibrations: the Bayer-Kushida (BK) model

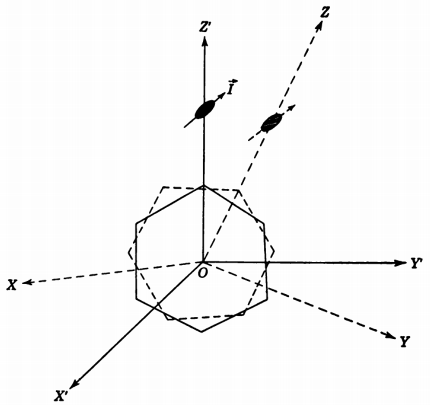

Figure : Bayer considered small rotations θ_x, θ_y, θ_z about each principle EFG axis

- Including terms up to second order in θ_x,θ_y,θ_z:

$$
\begin{array}{ccccccc}
\phi'_{xx} & = & \left(1-\theta_y^2-\theta_z^2\right)\phi_{xx} & + & \theta_z^2\phi_{yy} & + & \theta_y^2\phi_{zz} \\
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\phi'_{xy} & = & \theta_z\phi_{xx} & + & \left(\theta_x\theta_y-\theta_z\right)\phi_{yy} & - & \theta_x\theta_y\phi_{zz} \\
\phi'_{yz} & = & -\theta_y\theta_z\phi_{xx} & + & \theta_x\phi_{yy} & + & \left(\theta_y\theta_z-\theta_x\right)\phi_{zz} \\
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- $\langle\theta_x^2\rangle$, $\langle\theta_y^2\rangle$,$\langle\theta_z^2\rangle$ are all positive however

- Massaging, ϕ'_{zz} and η' are

$$\phi'_{zz} = \phi_{zz}\left[1 - \frac{3}{2}\left(\langle\theta_x^2\rangle + \langle\theta_y^2\rangle\right) - \frac{1}{2}\eta\left(\langle\theta_x^2\rangle - \langle\theta_y^2\rangle\right) + \frac{1}{2}(3-\eta)\langle\theta_x^2\rangle\langle\theta_y^2\rangle\right]$$

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T-dependence of NQR frequencies

Lattice vibrations: the Bayer-Kushida (BK) model

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- Image of NQR falling off with T

- The model goes on to replace each $\langle \theta_i^2 \rangle$ with harmonic oscillators summed over all the modes of the lattice

$$\frac{1}{A_i}\omega_i^2\langle\theta_i^2\rangle = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_i/kT} - 1}\right)$$

T-Dependence of NQR

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$$\nu_q\left(T\right) = \nu_0\left[1 - \frac{3}{2}\sum_{i=1}^{N}\frac{A_i}{\omega_i^2}\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_i/kT} - 1}\right)\right]$$

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- Consider only the first $M < N$ modes which satisfy $\hbar\omega_i \leq kT$
- Now expand

$$\frac{1}{2} + \frac{1}{e^{\hbar\omega_i/kT} - 1} = \frac{1}{x} + \frac{x}{12} + \mathcal{O}\left(x^3\right)$$

- The expansion is very accruate; only off by a few percent when $x = 2$

- Substituting the expansion into the expression for $\nu\left(T\right)$ we find

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T-Dependence of NQR

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- c;

$$c = \frac{\hbar^2}{8k} M \langle A \rangle$$

Failures of the model

a constant volume theory

- Model includes no volume dependence:
- the EFG depends on volume
- the phonon frequencies depend on volume

Outline

img/TNT-molecule.png

.png .pdf .jpg .mps .jpeg .jbig2 .jb2 .PNG .PDF .JPG .JPEG .JBIG2 .JB2 .eps

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- Outlook
  - Something you haven't solved.
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For Further Reading I

A. Author.
Handbook of Everything.
Some Press, 1990.

S. Someone.
On this and that.
Journal of This and That, 2(1):50–100, 2000.