

Module VI, Lecture 03: Spin Relaxation in Solid State

This lecture will describe spin relaxation caused by the coupling of spin degrees of freedom to the vibrational degrees of freedom of the crystal lattice. The primary mechanism (proposed initially by Van Vleck and elaborated upon in our context by Orbach) is the modulation of spin interactions by molecular vibrations – spin interactions depend on molecular geometry and the geometry displacement is a function of phonon population numbers in the lattice.

Quantization of vibrations

The Hamiltonian for a single harmonic oscillator of mass m with a spring force constant k is:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{kx^2}{2} \quad (1)$$

A standard variable substitution simplifies the notation:

$$\begin{cases} y = (m\omega/\hbar)^{1/2} x \\ \omega = (k/m)^{1/2} \end{cases} \Rightarrow \hat{H} = -\frac{\partial^2}{\partial y^2} + y^2 \quad (2)$$

The eigenfunctions of this Hamiltonian are the well-known Gaussian-weighted Hermite polynomials, which we will denote $|n\rangle$; their explicit form will not in practice be necessary. The eigenvalues of the Hamiltonian in Equation (2) are:

$$\hat{H}|n\rangle = E_n|n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega|n\rangle \quad (3)$$

It is convenient to define *raising and lowering operators* that would move a state up and down the excitation spectrum of the oscillator:

$$\begin{aligned} \hat{a}^\dagger &= \frac{i}{\sqrt{2}} \left(\frac{\partial}{\partial y} - y \right), & \hat{a} &= \frac{i}{\sqrt{2}} \left(\frac{\partial}{\partial y} + y \right) \\ \hat{a}|n\rangle &= \sqrt{n}|n-1\rangle, & \hat{a}^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle, & \hat{a}^\dagger\hat{a}|n\rangle &= n|n\rangle, & [\hat{a}, \hat{a}^\dagger] &= 1 \end{aligned} \quad (4)$$

Expressed in terms of raising and lowering operators, the Hamiltonian becomes:

$$\hat{H} = \hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger \quad (5)$$

An important object for the subsequent treatment is the *displacement operator*, corresponding to the original oscillator variable x from Equation (1):

$$x = \left(\frac{\hbar}{m\omega}\right)^{1/2} y = \dots = \frac{-i}{\sqrt{2}} \left(\frac{\hbar}{m\omega}\right)^{1/2} (\hat{a} - \hat{a}^\dagger) \quad (6)$$

This operator gives the displacement of the oscillator from the equilibrium point. In the more general case of multiple coupled harmonic oscillators we have:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \frac{\partial^2}{\partial r_i^2} + \frac{1}{2} \sum_{i,j} k_{ij} r_i r_j \quad (7)$$

where r_i is the displacement from the equilibrium position along the i -th Cartesian coordinate in the system and m_i is the mass of the corresponding particle. If the force constant matrix \mathbf{K} is diagonalized, the Hamiltonian acquires the following form:

$$\hat{H} = \sum_i \hat{H}_i, \quad \hat{H}_i = -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \rho_i^2} + \frac{k_i \rho_i^2}{2} \quad (8)$$

where m_i is the effective mass of i -th normal mode, k_i is its effective force constant (the eigenvalue of the force matrix) and the normal mode coordinates ρ_i are related to the Cartesian coordinates through the eigenvectors of the force matrix:

$$\mathbf{K}\vec{\kappa}^{(i)} = k_i \vec{\kappa}^{(i)}, \quad \rho_i = \sum_j \kappa_j^{(i)} r_j, \quad r_i = \sum_j \kappa_i^{(j)} \rho_j \quad (9)$$

We can now apply a transformation similar to the one in Equation (2) to simplify the notation:

$$\begin{cases} q_i = (m_i \omega_i / \hbar)^{1/2} \rho_i \\ \omega_i = (k_i / m_i)^{1/2} \end{cases} \Rightarrow \hat{H}_i = -\frac{\partial^2}{\partial q_i^2} + q_i^2 = \hat{a}_i^\dagger \hat{a}_i + \hat{a}_i \hat{a}_i^\dagger \quad (10)$$

where ω_i is the frequency of the i -th normal mode and $\hat{a}_i^\dagger, \hat{a}_i$ are the raising and lowering operators for its excitations:

$$\hat{a}_i^\dagger = \frac{i}{\sqrt{2}} \left(\frac{\partial}{\partial q_i} - q_i \right), \quad \hat{a}_i = \frac{i}{\sqrt{2}} \left(\frac{\partial}{\partial q_i} + q_i \right) \quad (11)$$

The displacement operator \hat{r}_i along the i -th Cartesian coordinate is defined by extending Equation (6):

$$r_i = \sum_j \kappa_i^{(j)} \rho_j = \sum_j \left(\frac{\hbar}{m_j \omega_j} \right)^{1/2} \kappa_i^{(j)} q_j = \frac{-i}{\sqrt{2}} \sum_j \left(\frac{\hbar}{m_j \omega_j} \right)^{1/2} \kappa_i^{(j)} (\hat{a}_j - \hat{a}_j^\dagger) \quad (12)$$

The sum in this expression runs over all normal modes in the system. The normal mode coefficient $\kappa_i^{(j)}$ may be viewed as a “weight” of the j -th normal mode in the i -th Cartesian coordinate displacement.

Three-dimensional crystal lattices

The matrix elements of the displacement \vec{u} from the equilibrium of a three-dimensional uniform crystal lattice at a specific point \vec{r} are given by (see Orbach’s papers for a detailed derivation):

$$\begin{aligned} \langle n_{\vec{q},s} - 1 | \vec{u}(\vec{r}) | n_{\vec{q},s} \rangle &= \sqrt{\frac{\hbar n_{\vec{q},s}}{2M \omega_{\vec{q},s}}} \vec{v}(\vec{q},s) e^{i(\vec{q} \cdot \vec{r})} \\ \langle n_{\vec{q},s} + 1 | \vec{u}(\vec{r}) | n_{\vec{q},s} \rangle &= \sqrt{\frac{\hbar (n_{\vec{q},s} + 1)}{2M \omega_{\vec{q},s}}} \vec{v}(\vec{q},s) e^{-i(\vec{q} \cdot \vec{r})} \end{aligned} \quad (13)$$

where \vec{q} is the phonon wave vector, s is the polarization index, $n_{\vec{q},s}$ is the occupation number of the normal mode with wave vector \vec{q} and polarization index s , $\omega_{\vec{q},s}$ is the frequency of that normal mode, $\vec{v}(\vec{q},s)$ is a unit vector in the direction of polarization and M is the mass of the crystal. In practice, we will use the strain tensor $\boldsymbol{\varepsilon}$ rather than displacements:

$$\varepsilon_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} \right), \quad \alpha, \beta = \{x, y, z\} \quad (14)$$

Skipping another lengthy derivation (see Orbach’s original papers), the squares of the matrix elements for the isotropic part of the lattice strain tensor are:

$$\left| \langle n_{\vec{q},s} - 1 | \varepsilon | n_{\vec{q},s} \rangle \right|^2 = \frac{\hbar q^2 n_{\vec{q},s}}{2M\omega_{\vec{q},s}}, \quad \left| \langle n_{\vec{q},s} + 1 | \varepsilon | n_{\vec{q},s} \rangle \right|^2 = \frac{\hbar q^2 (n_{\vec{q},s} + 1)}{2M\omega_{\vec{q},s}} \quad (15)$$

where q is the length of the wave vector \vec{q} . The matrix elements in Equation (15) refer to a specific normal mode – we will eventually need to take a sum over all modes.

One-phonon Orbach processes

Most spin interaction operators depend on molecular geometry and therefore on the local lattice strain. A given spin operator \hat{V} would therefore have a Taylor expansion in the powers of that strain:

$$\hat{V}(\varepsilon) = \hat{V}_0 + \hat{V}_1 \varepsilon + \hat{V}_2 \varepsilon^2 + \dots \quad (16)$$

The zero-order term is static and may be placed into the main spin Hamiltonian, the first-order term will be used as a perturbation. Higher terms will be ignored.

From the standard time-dependent perturbation theory, we get the following transition probabilities per unit time between two spin states $|b\rangle$ and $|a\rangle$:

$$W_{b \rightarrow a} = \frac{2\pi}{\hbar} \left| \langle \text{final} | \hat{V}_1 \varepsilon | \text{initial} \rangle \right|^2 \delta(E_{\text{initial}} - E_{\text{final}}) \quad (17)$$

where the “initial” and “final” labels refer to the state of the full system (spins + lattice), and the lattice states now need to be integrated over:

$$W_{b \rightarrow a} = \frac{2\pi}{\hbar} \frac{3Vn_b}{2\pi^2 v^3} \int \left| \langle a | \hat{V}_1 | b \rangle \right|^2 \left| \langle n_q + 1 | \varepsilon | n_q \rangle \right|^2 \delta(\hbar\omega_{ab} - \hbar\omega_q) \omega^2 d\omega \quad (18)$$

where v is the phonon velocity and V is the volume of the crystal. Using the matrix element from Equation (15) and assuming that the phonons that we are interested in have very low energy, we can replace ω_q by vq and take the integral:

$$W_{b \rightarrow a} = \frac{3\omega_{ab}^3}{2\pi\rho v^5 \hbar} \left| \langle a | \hat{V}_1 | b \rangle \right|^2 (n_{\omega_{ab}} + 1) n_b, \quad n_{\omega_{ab}} = \frac{1}{\exp(\hbar\omega_{ab}/kT) - 1} \quad (19)$$

and similarly:

$$W_{a \rightarrow b} = \frac{3\omega_{ab}^3}{2\pi\rho v^5 \hbar} \left| \langle a | \hat{V}_1 | b \rangle \right|^2 n_{\omega_{ab}} n_a \quad (20)$$

The net flux from $|b\rangle$ to $|a\rangle$ is the difference between $W_{b \rightarrow a}$ and $W_{a \rightarrow b}$ transition rates:

$$\frac{d}{dt}(n_b - n_a) = W_{b \rightarrow a} - W_{a \rightarrow b} = -\frac{3\omega_{ab}^3}{\pi\rho v^5 \hbar} \left| \langle a | \hat{V}_1 | b \rangle \right|^2 \left[(n_{\omega_{ab}} + 1) n_b - n_{\omega_{ab}} n_a \right] \quad (21)$$

after plugging in the thermodynamic expressions for the occupation numbers, we get:

$$\frac{1}{T_1} = \frac{3\omega_{ab}^3}{2\pi\rho v^5 \hbar} \left| \langle a | \hat{V}_1 | b \rangle \right|^2 \left(\frac{\exp(\hbar\omega_{ab}/kT) + 1}{\exp(\hbar\omega_{ab}/kT) - 1} \right) \quad (22)$$

assuming $\hbar\omega_{ab} \ll kT$, we can simplify this into:

$$\frac{1}{T_1} = \frac{3\omega_{ab}^2 kT}{\pi\rho v^5 \hbar^2} \left| \langle a | \hat{V}_1 | b \rangle \right|^2 \quad (23)$$

The resulting relaxation time is inversely proportional to temperature (hence the need for low temperatures in many solid-state EPR systems where relaxation is dominated by Orbach processes) and to the square of the spin energy level splitting – the relaxation is slower in lower field. Note the multiple approximations made above, particularly the $\hbar\omega_{ab} \ll kT$ assumption in Equation (23), and the fact that the spin operator matrix element $\langle a | \hat{V}_1 | b \rangle$ depends on the lattice strain response operator that is in practice impossible to compute.

Two-phonon Orbach processes

The single-phonon processes that we looked at in the previous lecture assumed that the energy of the participating phonons is very low, $\hbar\omega \ll kT$. We did, however, also see that the phonon occupation number density is:

$$n(\omega) \sim \frac{\omega^2}{\exp(\hbar\omega/kT) - 1} \quad (24)$$

which has a maximum around $\hbar\omega \sim kT$, meaning that the number of relatively high energy phonons in the system is much greater. On the strength of this fact, we could reasonably conclude that we ought to consider the second order in our perturbation treatment, which would involve phonons of all energies:

$$W_{b \rightarrow a} = \frac{2\pi}{\hbar} \left| \sum_{\text{intermediate states}} \frac{\langle \text{final} | \hat{V}_1 \varepsilon | \text{intermediate} \rangle \langle \text{intermediate} | \hat{V}_1 \varepsilon | \text{initial} \rangle}{E_{\text{init}} - E_{\text{interm}}} \right|^2 \delta(E_{\text{init}} - E_{\text{fin}}) \quad (25)$$

This is essentially a Raman process via all possible intermediate states that are summed over. After integrating over all phonon energies (see Orbach's original papers), we get:

$$\frac{1}{T_1} = \frac{9}{4\pi^3 \rho^2 v^{10}} \iint \left| \sum_t \left(\frac{\langle a | \hat{V}_1 | t \rangle \langle t | \hat{V}_1 | b \rangle}{\hbar\omega_1 - E_t} + \frac{\langle a | \hat{V}_1 | t \rangle \langle t | \hat{V}_1 | b \rangle}{-\hbar\omega_2 - E_t} \right) \right|^2 \omega_1^3 \omega_2^3 \frac{e^{\frac{\hbar\omega_1}{kT}} \delta(\omega_1 + \omega_{ab} - \omega_2)}{(e^{\frac{\hbar\omega_1}{kT}} - 1)(e^{\frac{\hbar\omega_2}{kT}} - 1)} d\omega_1 d\omega_2 \quad (26)$$

Assuming that $\hbar\omega_{ab} \ll kT$ and $E_t \gg kT$, the integral evaluates approximately to:

$$\frac{1}{T_1} = \frac{1620}{\pi^3 \rho^2 v^{10}} \left(\frac{kT}{\hbar} \right)^7 \left| \sum_t \frac{1}{E_t} (\langle a | \hat{V}_1 | t \rangle \langle t | \hat{V}_1 | b \rangle + \langle a | \hat{V}_1 | t \rangle \langle t | \hat{V}_1 | b \rangle) \right|^2 \quad (27)$$

where, just as in Equation (23), the terms under the sum are next to impossible to evaluate because the first-order lattice strain response spin operator \hat{V}_1 is very unlikely to be known. Still, we can conclude that this contribution to spin relaxation rate depends on the seventh power of temperature and does not depend on the spin energy level splitting.