Relaxation of muonium states in solids

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The dipole interaction between a muon, which forms a paramagnetic state in a solid, and neighboring nuclei leads to a relaxation of the hyperfine oscillations which are observed in transverse magnetic field experiments. It is shown how the damping rates, which depend on the superhyperfine interaction and the strength and orientation of the external field, can be calculated. An explicit expression for the relaxation function of anomalous muonium is derived which is valid for high fields and negligible quadrupole interactions. The determination of the muon site in the general case and the relaxation function of normal muonium are discussed.

Positive muons stopped in insulators may form paramagnetic centers. The number of substances where isotropic (normal) muonium, anisotropic (anomalous) muonium, or both states have been observed and their hyperfine parameters measured has recently increased dramatically as a result of the use of novel and improved experimental techniques.[1-4] The sites in the crystal lattice of these hydrogenlike centers are, however, still unknown, which prevents a reasonable discussion of their electronic structure.

Information about the sites can, in principle, be obtained from detecting level-crossing resonances in longitudinal fields,[5] and first results[6] look promising, although the unknown interactions of the electron with the nuclei (superhyperfine interaction) and the quadrupole and dipole energy render an unambiguous interpretation of the data difficult.

The purpose of the present contribution is to point out that measurements of the relaxation rates of muonium transitions in high transverse fields could yield all information about the superhyperfine interaction parameters and the dipole interaction required for a site determination. Such experiments would thus provide complementary results to those obtained from level-crossing data. The general theory is illustrated by an explicit calculation of the relaxation functions for anomalous muonium, which under certain approximations can be evaluated analytically.

Let H denote the spin Hamiltonian describing the paramagnetic muonium center and the interaction of the electron with one or several nuclei, and H_D the dipolar coupling between the muon and the nuclear moments. If the transformation which diagonalizes H is written as

$$\tilde{H} = U^\dagger H U \ , \tag{1}$$

the secular part of the transformed dipolar interaction is given by

$$\tilde{H}_D^{\text{sec}} = \text{diag}(\tilde{H}_D) = \text{diag}(U^\dagger H_D U) \ . \tag{2}$$

This diagonal part yields a small splitting of the transition frequencies which causes a broadening of the muonium lines.

As an illustration, we consider in the following the particular case of anomalous muonium interacting with a single nucleus in an approximation which allows an analytic calculation. The result, however, is general enough to be directly applicable to the interpretation of a variety of possible experiments. The Hamiltonian is written as

$$H = H_{I\text{-}S} + H_{J\text{-}S} + H_Z \ , \tag{3}$$

where

$$H_Z = -\gamma_\mu I^z B - \gamma_J J^z B + \gamma_e S^z B \tag{4}$$

describes the Zeeman terms of the spins of the muon I, the nucleus J, and the electron S, respectively. The anisotropic interaction of the muon and the electron is given by

$$H_{I\text{-}S} = \nu \mathbf{I}\cdot\mathbf{S} + \delta(\hat{\mathbf{n}}\cdot\mathbf{I})(\hat{\mathbf{n}}\cdot\mathbf{S}) \ , \tag{5}$$

where

$$\hat{\mathbf{n}} = (\sin\theta, 0, \cos\theta) \ , \tag{6}$$

and the interaction between the electron and the nucleus is written as

$$H_{J\text{-}S} = \nu' \mathbf{J}\cdot\mathbf{S} + \delta'(\hat{\mathbf{k}}\cdot\mathbf{J})(\hat{\mathbf{k}}\cdot\mathbf{S}) \ , \tag{7}$$

with

$$\hat{\mathbf{k}} = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta) \ . \tag{8}$$

$H_{J\text{-}S}$ can describe the superhyperfine interaction or the dipole interaction of a localized electron with a nucleus. We neglect here any quadrupole interaction of the nucleus J since electron-nuclear double resonance measurements on hydrogen centers in alkali halides show these quadrupole energies to be rather small.[7]

For sufficiently high field strength B the electron spin can be assumed to be frozen either parallel $(-)$ or antiparallel $(+)$ to the field. This approximation, which is well justified in most cases as can easily be checked numerically,[8] leads to a decoupling of the Hamiltonian H into H_+ and H_-:

$$H_\pm = -\gamma_\mu \mathbf{I}\cdot\mathbf{F}_\pm - \gamma_J \mathbf{J}\cdot\mathbf{G}_\pm \ , \tag{9}$$

where the spins of the muon and the nucleus are subject to effective fields $\mathbf{F}_{\pm}$ and $\mathbf{G}_{\pm}$, respectively, with components

$$F^x_{\pm} = \pm \delta \sin\theta \cos\theta / 2\gamma_\mu ,$$
$$F^z_{\pm} = B \pm (\nu + \delta \cos^2\theta)/2\gamma_\mu ,$$
$$G^x_{\pm} = \pm \delta' \cos\vartheta \sin\vartheta \cos\varphi / 2\gamma_J , \quad (10)$$
$$G^y_{\pm} = \pm \delta' \cos\vartheta \sin\vartheta \sin\varphi / 2\gamma_J ,$$
$$G^z_{\pm} = B \pm (\nu' + \delta' \cos^2\vartheta)/2\gamma_J .$$

The transformation which diagonalizes $H_{\pm}$ in the standard representation can now simply be written as a product of rotations,

$$U_{\pm} = \exp(-i\alpha_{\pm} I^y)\exp(-i\varphi J^z)\exp(-i\beta_{\pm} J^y) , \quad (11)$$

where the rotation angles α and β are given by

$$\alpha_{\pm} = \arctan(F^x_{\pm}/F^z_{\pm}) , \quad (12)$$
$$\beta_{\pm} = \arctan[(G^x_{\pm} \cos\varphi + G^y_{\pm} \sin\varphi)/G^z_{\pm}] . \quad (13)$$

In this way one obtains the diagonalized Hamiltonian

$$\tilde{H}_{\pm} = U^{\dagger}_{\pm} H_{\pm} U_{\pm} = -\gamma_\mu I^z |\mathbf{F}_{\pm}| - \gamma_J J^z |\mathbf{G}_{\pm}| \quad (14)$$

and the precession frequencies of the muon

$$\nu^2_{\pm} = [\gamma_\mu B \pm 0.5(\nu + \delta \cos^2\theta)]^2 + 0.25\delta^2 \sin^2\theta \cos^2\theta . \quad (15)$$

The dipolar interaction between the muon and the nucleus is written as

$$H_D = \nu_D [\mathbf{I}\cdot\mathbf{J} - 3(\hat{\mathbf{m}}\cdot\mathbf{I})(\hat{\mathbf{m}}\cdot\mathbf{J})] , \quad (16)$$

where $\hat{\mathbf{m}}$ denotes the unit vector in the direction from the muon site to the nucleus. The secular part of H_D can then be calculated according to Eq. (2) with the result

$$\tilde{H}^{\text{sec}}_{D\pm} = \text{diag}(\tilde{H}_{D\pm}) = \nu_D I^z J^z K(\alpha_{\pm}, \beta_{\pm}; \varphi, \hat{\mathbf{m}}) , \quad (17)$$

where

$$K(\alpha_{\pm},\beta_{\pm};\varphi,\hat{\mathbf{m}}) = \cos\alpha_{\pm} \cos\beta_{\pm} + \sin\alpha_{\pm} \sin\beta_{\pm} \cos\varphi - 3[(\hat{m}_x \sin\alpha_{\pm} + \hat{m}_z \cos\alpha_{\pm})(\hat{m}_x \sin\beta_{\pm} \cos\varphi + \hat{m}_y \sin\beta_{\pm} \sin\varphi + \hat{m}_z \cos\beta_{\pm})] . \quad (18)$$

Since the dipolar frequencies are small compared to the hyperfine frequencies, the effect of the secular dipole interaction is, as usual,[9] expressed in the form of a Gaussian relaxation function. Therefore, the time dependence of the transverse muon polarization is written as

$$p^x_{\pm}(t) = \tfrac{1}{2}[\sin^2\alpha_{\pm} + \cos^2\alpha_{\pm} \cos(2\pi\nu_{\pm} t)\exp(-\tfrac{1}{2}R_{\pm} t^2)], \quad (19)$$

where

$$R_{\pm} = \tfrac{1}{3}(2\pi\nu_D)^2 J(J+1) K^2(\alpha_{\pm},\beta_{\pm};\varphi,\hat{\mathbf{m}}) . \quad (20)$$

An inspection of these equations shows that in the extreme high-field limit where $\alpha_{\pm}$ and $\beta_{\pm}$ vanish, the usual expression for the second moment which only depends on ν_D and m_z is obtained. In general, however, the relaxation rates for anomalous muonium are, through α and β, also field dependent and differ for the two frequencies. Therefore, it is, in principle, possible to determine all parameter values ν', δ', ν_D as well as the vectors $\hat{\mathbf{k}}$ and $\hat{\mathbf{m}}$ from a comparison of a set of data with the above expressions.[10]

The contributions of several nuclei to the second moment are simply additive, at least as long as the approximation of neglect of the dynamics of the electron spin is justified. Thus the theory developed can be helpful for the interpretation of relaxation experiments on muonium or anomalous muonium in group-III-V compound semiconductors or in alkali halides; in particular, in cases where the superhyperfine interactions with only one or two nuclei are dominant.[11] The other nuclei neighboring the muon are then subject to a dipole field produced by the localized electron. Their contribution can also be calculated from the general equations above by putting $\delta' = -3\nu'$. To account for a possible quadrupole interaction of the nucleus J, a simple numerical evaluation of that part of the transformation matrix U which involves the nuclear spin J is needed.

The results for the relaxation function are, of course, also valid for normal muonium ($\delta = 0$ and $\alpha_{\pm} = 0$) provided that the external field is high enough to justify the neglect of the spin dynamics of the electron. For hyperfine frequencies near the vacuum value ($\nu \sim 4400$ MHz) this would require fields on the order of 2 T. This in turn implies very high frequencies of the precession signals, whose small relaxation due to ν_D cannot be detected with the present experimental resolution. For lower fields, there is an additional broadening of the muonium frequency lines due to the superhyperfine and quadrupole interactions of the nuclei. This general case can be treated according to Eqs. (1) and (2) by calculating the secular parts of the combined dipole and superhyperfine interactions.

It is evident that all the arguments given in the present contribution only apply to static muonium centers without additional incoherent relaxation mechanisms as spin exchange with charge carriers or spin flips due to phonon processes. This limits the applicability of the results to a certain temperature range. The onset of diffusion or relaxation of the electronic moment will lead to different relaxation functions for the muon, which, however, will in general not depend on the crystal orientation. On the other hand, an interpretation of the mechanisms leading to dynamical relaxation greatly benefits from an understanding of the static situation.

In conclusion, it has been shown that the relaxation of the hyperfine oscillations due to the dipole interaction between the muon and nuclei strongly depends on the local geometric structure of the muonium center, the superhyperfine interaction, and the strength and direction of the external field. This allows experimentalists to obtain the information about the muon site and the superhyperfine parameters which is necessary to make a microscopic theory of the electronic structure of the muonium centers feasible.

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[8]P. F. Meier, in *Exotic Atoms 1979: Fundamental Interactions and Structure of Matter,* edited by K. Crowe *et al.* (Plenum, New York, 1980).

[9]See, e.g., A. Abragam, *The Principles of Nuclear Magnetism* (Oxford Univ. Press, Oxford, England, 1961).

[10]The feasibility of measuring the relaxation rates depends, of course, on the magnitude of v_D, which is very small if the muon happens to be at a vacancy. In this case, however, it could at least be possible to exclude experimentally other sites which then would lead indirectly to a site determination.

[11]The dilute occurrence of nuclei with nonvanishing magnetic moments in the elemental semiconductors Si, Ge, and diamond leads to a strong reduction of the observable relaxation effects, which probably prohibits an experimental detection.