Electron Paramagnetic Resonance and Electrically Detected Magnetic Resonance

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1 Electron Paramagnetic Resonance (EPR)

1.1 Zeeman Effect

The intrinsic $|\frac{1}{2}, m_s \in \{\frac{1}{2}, -\frac{1}{2}\}\rangle$ spin of an electron gives rise to an electron's magnetic moment.

$$\vec{\mu}_e = \gamma \vec{S} = g_e \mu_B \vec{S}.$$

where μ_e is the magnetic moment of the electron, γ is the gyromagnetic ratio, g_e is the Lande factor, and μ_B is the Bohr magneton.

For an unperturbed electron, the Hamiltonian is given by

$$H = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{B} \cdot S.$$

Therefore, the energy levels can be computed via

$$E = -\vec{\mu}_e \cdot \vec{B} = g \mu_B \vec{S} \cdot \vec{B}.$$

In a reference frame aligned with the magnetic field $\vec{B}$, the equation simplifies to

$$E = -\vec{\mu}_e \cdot \vec{B} = g_e \mu_B S_Z B_0$$

where S_Z is the magnitude of the electron spin projected onto the z axis ($+1/2$ or $-1/2$) and B_0 is the strength of the $\vec{B}$ field in the z direction. Hence, there exists an energy difference between electrons of different spin orientations.

$$\Delta E = g_e \mu_B B_0.$$

This is known as the *Zeeman Effect*. The energy splitting is proportional to the applied magnetic field. Electrons in one of these states can absorb and release energy to switch, or 'flip' between spin states.

In EPR, this is achieved by exposing the electron to electromagnetic radiation. The resonance energy required to flip an isolated electron is given by

$$\Delta E = h\nu = g_e \mu_B B_0.$$

However, this is for a free electron isolated from its surroundings. Unpaired electrons in real materials deviate from this idealized situation.

1.2 EPR Response

In conventional EPR, a sample with paramagnetic centers is placed into a microwave cavity of high quality/Q factor. A standing wave is set up in this cavity to provide an oscillating B field of frequency ν. The cavity is placed in a large slowly varying magnetic field. Resonance is detected when the applied microwave radiation is absorbed by the sample, causing the Q factor of the cavity to change.

The change in Q causes a change in the reflected power back to a diode in the microwave bridge. An absorption spectrum is measured when the reflected microwave power is plotted against the slowly varying magnetic field.

In a perfectly balanced system (infinite spin temperature) where there are an equal number of spin up and spin down state, stimulated emission and absorption would occur at the same rate and cancel each other. Hence, measuring the EPR response is related to the spin polarization.

The ratio of the number of spins in the up and down state for free and isolated electrons can be approximated by

$$\frac{N_+}{N_-} = \exp\left(\frac{-g_e\mu_B B_0}{k_B T}\right) \approx 1 - \frac{g_e\mu_B B_0}{k_B T}.$$

Hence, increasing B_0 and decreasing T increases spin polarization. This ratio is approximately 1 if the Lande factor for the detect in question is close to free electron, implying there is an equal balance of spin up and spin down. This level of polarization is still high enough to detect approximately 10^10 paramagnetic sites.

1.3 Spin Relaxation

As spins flip due to exposure to radiation satisfying the resonance condition, they also interact with their local environment. Electron spins can return to their original state via spin relaxation.

The time it takes for a spin system out of equilibrium to relax back to its equilibrium is described by spin-lattice-relaxation time, T_1. Increased electron coupling to the lattice results in lower T_1. Electron spins can interact with each other causing them to precess at slightly different rates, becoming de-phased over a spin-spin relaxation time, T_2.

1.4 Spin Orbit Coupling

The electron's magnetic moment is described by both terms,

$$\vec{\mu}_e = g\mu_B\vec{S} + \mu_B\vec{L}.$$

The electron 'orbiting' the nucleus acts as a small current loop which in turn generates its own magnetic field around the loop. However, in the electron frame, the nucleus is the one revolving

around *it*, which alters this magnetic moment. This is called *spin-orbit coupling.*

The amount of spin-orbit coupling experienced is measured as a change in the g. The $\vec{g}$ factor is a second-rank tensor that is anisotropic.

$$\vec{g} = \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix}.$$

1.5 Hyperfine Interactions

Atomic nuclei can also possess spin angular momentum, though not all do. The spin angular momentum, $\vec{I}$ alters the resonance condition of an electron in a paramagnetic site. Unlike electrons, which all have spin 1/2, the nuclear spin depends on the # of protons and neutrons in the nucleus. The magnetic moment of the nuclear spin angular momentum is described by

$$\vec{\mu}_N = g_N \mu_N \vec{I}$$

where g_N is the nuclear g factor, and μ_N is the nuclear Bohr magneton. A paramagnetic electron close to a nucleus with a nuclear magnetic moment experiences a local magnetic field from the nucleus that differs from the externally applied field. The interaction between electrons and nearby magnetic nuclei is known as the *nuclear hyperfine interaction* and is characterized by a splitting of the measured EPR spectrum into two or more lines. The Hamiltonian then becomes

$$\hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} + \sum_i \vec{I}_i \cdot \vec{A}_i \cdot \vec{S}.$$

where $\vec{I}_i$ is the nuclear spin operator for each nucleus and $\vec{A}_i$ is the hyperfine tensor for each nucleus.

1.6 EDMR

The most common EDMR experiments involve changes in spin dependent currents due to recombination or tunneling. This has higher sensitive, with orders-of-magnitude less defects.

The detection scheme for EDMR relies on changes in the electrical characteristics of a sample as it undergoes magnetic resonance. An electrical connection must be made to the sample in the microwave cavity and a current-to-voltage converter is used with a biasing circuit.

Measured EDMR spectra are generated by plotting the change in the electrical current through the sample as a function of the slowly varied magnetic field, B_0. The two primary spin dependent currents measured are spin-dependent recombination (SDR) and spin-dependent trap assisted tunneling (SDTAT).

1.7 Spin Dependent Recombination

Electrons and holes can be captured by deep level defects within the bandgap. When an electron in the conduction band and an electron in a paramagnetic defect are polarized in the same direction, the conduction band electron cannot be captured due to the Pauli-Exclusion Principle.

The electron in the trap can be flipped during magnetic resonance, converting what was a triplet state into a singlet state, making the previously forbidden transition possible. The conduction electron can now be captured by the deep level defect and recombine with a hole from the valence band. An increased number of recombination events during magnetic resonance causes a measurable change in the steady state current.

1.8 Spin Dependent Trap Assisted Tunneling

SDTAT is an EDMR measurement that relies on the spin-dependent nature of VRH currents, where electrons can hope between localized states via quantum tunneling. Electrons cannot tunnel to a site with a same polarized electron however. The electron can be flipped at magnetic resonance, thus allowing it to tunnel to the next site. This change in tunneling current through the material is measured during SDTAT and gives rise to the EDMR spectra associated with defects.

2 NZFMR Mechanics

The density operator for a simple two-site model with an ensemble of N spins can be written as:

$$\rho = \frac{1}{N} \sum_{n=1}^{N} |\psi_N\rangle\langle\psi_N|.$$

Choosing an orthonormal basis set φ_i allows us to define the density matrix as:

$$\rho_{i,j} = \langle\varphi_i|\rho|\varphi_j\rangle.$$

The system evolves coherently over time as the spins precess according to the time-dependent Schrodinger equation and is described by the quantum Liouville equation:

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}, \rho\right].$$

For a system in which spin pairs are formed and removed over time, it is necessary to include these phenomena in the equation governing the time evolution of the system. This is achieved by using the stochastic Liouville equation (SLE):

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[H, \rho] - \frac{1}{2}\{\Lambda, \rho\} + \Gamma.$$

where $\{\Lambda, \rho\}$ is the anticommutator of the projection operator Λ and ρ. The first term is the coherent time evolution with no perturbations. The second term is a dissipative term that removes spin pairs from the system. The last term is a generation term.

2.1 Electron-Hole SDR for NZFMR

An electron in the conduction band approaches a deep level defect with an unoccupied electron near a nucleus of nuclear spin and an associated hyperfine field.The free electron can be temporarily captured in an intermediate state just below the conduction band where it can *attempt* to enter the defect. If the free electron and defect electron are a singlet state, the free electron can be captured. Unlike in EDMR, the transition from triplet to singlet does not come from impinging electromagnetic radiation, but from spin mixing of the defect electron due to local magnetic fields.

If a singlet is formed due to spin mixing, the free electron drops into the deep levels and recombines with a hole in the valence band, removing the electron and hole from the system. This essentially annihilates the spins, hence an additional requirement for defect and free electron spins to be antiparallel – spin angular momentum conservation.