Electron Spin Resonance

Consider unpaired ~~electrons~~ non-interacting electrons.
Each of them has spin 1/2, and an associated magnetic moment:

$$\hat{\vec{M}} = -g\mu_B \hat{\vec{S}}/\hbar$$

[The hat implies a quantum mechanical operator, the operator can be a vector as well, having 3 components]

$$\mu_B = \frac{e\hbar}{2m} = 5.79\times10^{-4}\,eVT^{-1} \text{ (Bohr magneton)}$$

$$\hat{\vec{S}} = \frac{\hbar}{2}\hat{\vec{\sigma}} \text{ where } \hat{\vec{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$$

g; Landé g-factor

[aside: If the particles were nucleon, then the corresponding μ is called nuclear magneton, and $\hat{\vec{S}}$ would be replaced by nuclear isospin. The corresponding phenomenon is: Nuclear magnetic resonance (NMR)]

Getting back to the electronic system, the Hamiltonian for such system in a magnetic field is given by:

$$\hat{\mathcal{H}} = -\hat{\vec{M}}\cdot\vec{B} = -g\mu_B\frac{1}{\hbar}\hat{\vec{S}}\cdot\vec{B}$$

i.e., the ~~interaction between~~ the magnetic moments in the magnetic field gives rise to an energy:

$$U = -\vec{M}\cdot\vec{B} = g\mu_B m_s B \quad , \quad m_s = \pm 1/2 \text{ for}$$

electron's spin qtm. number.

So far we considered only the spin to contribute to electron's angular momentum. In general, electron can have orbital angular momentum as well, so that, the total angular momentum is: $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$, with eigenvalues:

"j" that goes from $(l-s)$ to $(l+s)$

(consult qtm. mech. book.)

The general expression for Landé g-factor is:

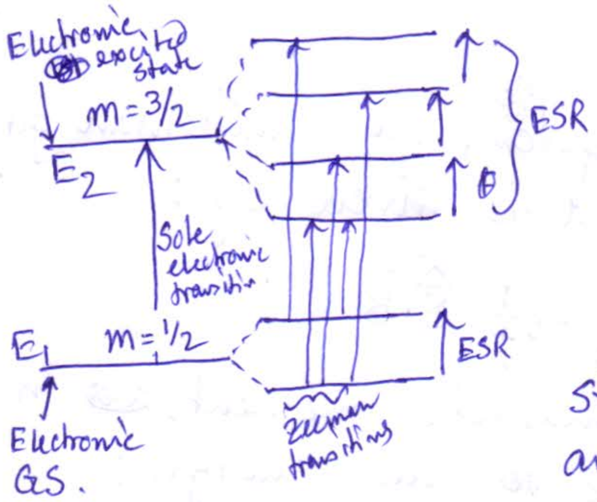
$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

which takes a value 2 for $l=0$ (so that $j=s$).

Let us assume, for now, that the magnetic field is pointing to $\hat{z}$-direction, so that:

$$\mathcal{H} = -g\,\mu_B \frac{1}{\hbar}\hat{S}_z B$$

Consider, an atom that carries such unpaired, non-interacting "spins" as electrons. ~~Let this have~~ Let the Ground State be identified by $m_s = 1/2$ and sole excited state by $m = 3/2$.



Then, only a single transition can be induced by absorption of radiation of frequency: (In the absence of external magnetic field)

$$\omega = (E_2 - E_1)/\hbar$$

Because the energy of the electronic state does not depend on the spin angular momentum, the GS is doubly degenerate, corresponding to $m_s = \pm 1/2$ of $\hat{S}_z$, and the excited state is quadruply degenerate corresponding to $m_s = +3/2, +1/2, -1/2, -3/2$ of $\hat{S}_z$. The magnetic field breaks such degeneracy by splitting the GS in 2-sublevels & the ES to 4-sublevels, called Zeeman Splitting.

Now, instead of a single transition with freq. $\omega = (E_2 - E_1)/\hbar$, several transitions with frequency close to ω are possible (See Fig.). This is Zeeman Effect.

However, there are now transition possible between sublevels too (of the same ~~ener~~ electronic energy level). This phenomenon gives rise to ESR.

Because ESR involves transitions only between sublevels of one (original) electronic level, we do not need to consider the detailed Hamiltonian for the atom / molecule, or even the parts that gives rise to the electronic levels, but consider only the terms of the Hamiltonian that generate the sublevels and transitions between them.

Because our real system ~~has~~ (DPPH) has just one unpaired electron, $\mathcal{H}_0 = -g \mu_B \frac{B}{\hbar} \hat{S}_z$

We then turn on an additional AC magnetic field of frequency ω, in a direction perpendicular to $\vec{B}$. (here B_z). Hence this new AC field lies in XY-plane.

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{V} \cos \omega t$$

When the new AC magnetic fld is weak (i.e. $\hat{V}$ is small compared to $\mathcal{H}_0$ [pl. understand the meaning of an operator being smaller than another!]), we can treat it as perturbation and obviously we have to use time-dependent pert. theory. The unperturbed states are $|m_z\rangle$, s.t. $\hat{S}_z |m_z\rangle = \hbar m_s |m_z\rangle$

$m_s = \pm 1/2$ here, whose energies are:

$$g \mu_B \frac{B}{\hbar} \hat{S}_z |m_z\rangle = \mathcal{E}_m |m_z\rangle \quad || \quad \mathcal{E}_m = g \mu_B \frac{B}{\hbar} m_s$$

Note that $V \propto \sigma_x$ or σ_y i.e. $V \sim \sigma^+$ or σ^-

which raises or lowers the spin of the unperturbed states and thereby causes transitions.

The transition rates are given by Fermi Golden Rule:
$$W_{1\to 2} = \frac{2\pi}{\hbar}\left|\langle 2|V|1\rangle\right|^2 \delta(\varepsilon_2 - \varepsilon_1 - \hbar\omega)$$

assumed $\varepsilon_2 > \varepsilon_1$

Also, the selection rule (that comes from the principle of conservation of angular momentum) ensures that the transition only occurs when $\Delta m_s = \pm 1$ [This is of course guarranteed for our case, where only two ~~two~~ Zeeman levels are with $m_s = \pm 1/2$]

... treatment of spin-flip

Consider single spin-$\frac{1}{2}$ with magnetic moment $\vec{M}$, described by its instantaneous state $\chi(t)$ (in the eigenbasis of σ_z), is put into a magnetic field $\vec{B} = (B_x, B_y, B_z)$.

Schrödinger eq^n:

$$i\hbar \frac{d\chi(t)}{dt} = -\hat{\vec{M}}.\vec{B}\,\chi(t)$$

$$= \frac{g\mu_B}{\hbar}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}\chi(t) \quad \text{--- (1)}$$

where we used $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$; $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$; $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Let, $\chi(t) = \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}$.

$B_z = B_0$ (external DC field) $\quad B_x = B_1 \cos(\omega t)$
~~Let the perturbation be~~ $\quad B_y = B_1 \sin(\omega t)$

Define: $\omega_0 = g\frac{\mu_B}{\hbar}B_0$; $\omega_1 = g\frac{\mu_B}{\hbar}B_1$

Then, the Schrödinger eq^n (1) becomes:

$$\left.\begin{aligned} \frac{da(t)}{dt} &= -i\omega_0 a(t) - i\omega_1 b(t) e^{-i\omega t} \\ \frac{db(t)}{dt} &= i\omega_0 b - i\omega_1 a(t) e^{+i\omega t} \end{aligned}\right\} \text{--- (2)}$$

We have to solve (2) with appropriate initial cond^n:

Suppose, at $t=0$, the electron occupies the lower level that correspond to "spin-down". i.e. $\chi(t=0) = \begin{pmatrix} a(0) \\ b(0) \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

i.e. Prob$_{\downarrow}(t=0) = 1$

We have to solve ② with above initial cond^n; and will learn about the transition by calculating $P_{\uparrow}(t) = |a(t)|^2$

& $P_{\downarrow}(t) = |b(t)|^2$

By solving ② we get [details not shown]

$$P_{\uparrow}(t) = |a(t)|^2 = \frac{\omega_1^2}{\omega_1^2 + (\omega_0 - \omega)^2} \sin^2(\delta t)$$

where $\delta = \sqrt{\omega_1^2 + (\omega_0 - \omega)^2}$

Averaged over long time $\langle \sin^2(\delta t) \rangle_{t\to\infty} = 1/2$

Thus the absorbed energy is proportional to

$$\frac{\omega_1^2}{\omega_1^2 + (\omega_0 - \omega)^2}$$

This is generally small [As $\omega_1 \ll \omega_0$ chosen for pert. theory to be valid]

unless $\omega_0 \simeq \omega$. [Resonance].

Please verify the algebra!
It might contain missed factors)