

330(7) : Conventional ESR and Conventional Spin-Orbit ESR.

The conventional ESR term is obtained from the main kinetic energy term:

$$H_{\text{ESR}} = \frac{p^2}{2m} \quad - (1)$$

where p is the relativistic momentum:

$$\underline{p} = \gamma \underline{p}_0 \quad - (2)$$

Now introduce the SU(2) basis:

$$H_{\text{ESR}} = \frac{1}{2m} \underline{\sigma} \cdot \underline{p} \underline{\sigma} \cdot \underline{p} \quad - (3)$$

where $\underline{\sigma}$ are the Pauli matrices, and use the minimal prescription:

$$H_{\text{ESR}} = \frac{1}{2m} \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \quad - (4)$$

to represent interaction w/ the electromagnetic field.

Quantization is introduced as follows:

$$\begin{aligned} H_{\text{ESR}} \psi &= \frac{1}{2m} \underline{\sigma} \cdot (-i\hbar \underline{\nabla} - e\underline{A}) \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \psi \\ &= \frac{i e \hbar}{2m} \underline{\sigma} \cdot \underline{\nabla} \underline{\sigma} \cdot \underline{A} \psi + \dots \quad - (5) \end{aligned}$$

From Pauli algebra:

$$\underline{\sigma} \cdot \underline{\nabla} \underline{\sigma} \cdot \underline{A} = \underline{\nabla} \cdot \underline{A} + i \underline{\sigma} \cdot \underline{\nabla} \times \underline{A} \quad - (6)$$

So the real part of the Hamiltonian is:

$$\text{Re } H_{\text{ESR}} \psi = -\frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{\nabla} \times \underline{A} \quad - (7)$$

$$= -\frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}$$

where

$$\underline{B} = \underline{\nabla} \times \underline{A} \quad - (8)$$

Resonance occurs between the states of $\underline{\sigma}$. With conventional magnet technology this can occur at up to tens of kHz frequencies.

The above is the simplest type of theory.

The conventional ESR line is split by spin orbit interaction. This originates in the spin orbit Hamiltonian which in the conventional Dirac approximation is:

$$H_{\text{SO}} = \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \frac{U}{4m^2c^2} \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \quad - (9)$$

where

$$U = -\frac{e^2}{4\pi\epsilon_0 r} \quad - (10)$$

i.e. the potential energy between an electron and proton in an atom. In Eq. (9), \underline{p} is again the relativistic momentum.

Quantization of eq. (9) takes place as follows:

$$\begin{aligned}
 H_{so} \psi &= \underline{\sigma} \cdot (-i\hbar \underline{\nabla} - e\underline{A}) \frac{U}{4m^2c^2} \underline{\sigma} \cdot (\underline{p} - e\underline{A}) \psi \quad (11) \\
 &= \left(-\frac{i\hbar}{4m^2c^2} \underline{\sigma} \cdot \underline{\nabla} U \underline{\sigma} \cdot (\underline{p} - e\underline{A}) + \dots \right) \psi \\
 &= \left(\frac{ie\hbar}{4m^2c^2} \underline{\sigma} \cdot \underline{\nabla} (U \underline{\sigma} \cdot \underline{A}) + \dots \right) \psi \\
 &= \frac{ie\hbar}{4m^2c^2} \left(\underline{\sigma} \cdot \underline{\nabla} U \underline{\sigma} \cdot \underline{A} + U \underline{\sigma} \cdot \underline{\nabla} \underline{\sigma} \cdot \underline{A} \right) \psi + \dots \quad (12)
 \end{aligned}$$

using the Leibnitz theorem.

The two terms in eq. (12) give rise to different types of spectroscopy.

Type One : Spin Orbit Term

$$H_{so1} \psi = \frac{ie\hbar}{4m^2c^2} \underline{\sigma} \cdot \underline{\nabla} U \underline{\sigma} \cdot \underline{A} \psi \quad (13)$$

where

$$\underline{\nabla} U = -\frac{e^2}{4\pi\epsilon_0 r^3} \underline{r} \quad (14)$$

$$\text{so: } \text{Re } H_{so1} \psi = \frac{-e^3 \hbar}{16\pi\epsilon_0 m^2 c^2 r^3} \underline{\sigma} \cdot \underline{r} \times \underline{A} \quad (15)$$

4) Define :

$$\underline{L}_{ind} = e \underline{r} \times \underline{A} \quad - (16)$$

to be the electronic angular momentum induced by the electromagnetic field. This is a kind of inverse Faraday effect. The induced magnetic dipole moment is:

$$\underline{m}_{ind} = -\frac{e}{2m} \underline{L}_{ind} \quad - (17)$$

Therefore :

$$Re H_{so} \psi = \frac{-e^2 \hbar}{16\pi \epsilon_0 m^2 c^2 r^3} \underline{\sigma} \cdot \underline{L}_{ind} \quad - (18)$$

This has the same structure as the conventional spin orbit Hamiltonian that leads to fine structure in atoms and molecules, but \underline{L} of an atom is replaced by \underline{L}_{ind} and the induced magnetic dipole moment \underline{m}_{ind} .

If it is assumed that :

$$\underline{L}_{ind} \psi = m \hbar \psi \quad - (19)$$

and

$$L_{ind}^2 \psi = L(L+1) \psi \quad - (20)$$

3) The same type of spin orbit structure appears as observed in atoms and molecules.

In terms of the magnetic dipole moment:

$$Re H_{so1} = \frac{e\hbar}{8\pi\epsilon_0 mc^2 r^3} \underline{\sigma} \cdot \underline{m}_{ind} \quad - (21)$$

and if \underline{m}_{ind} is regarded as classical then:

$$\langle Re H_{so1} \rangle = \frac{e\hbar}{8\pi\epsilon_0 mc^2} \left\langle \frac{1}{r^3} \right\rangle \underline{\sigma} \cdot \underline{m}_{ind} \quad - (22)$$

In Q. H atom:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0^3 L(L+\frac{1}{2})(L+1)n^3} \quad - (23)$$

where a_0 Bohr radius is:

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^4} \quad - (24)$$

This gives the first new type of ESR spectroscopy.

Type Two

This is given by the second term on the right hand side of eq. (12)

$$H_{so2} = \frac{ie\hbar U}{4m^2 c^2} \underline{\sigma} \cdot \underline{\nabla} \underline{\sigma} \cdot \underline{A} \quad - (25)$$

3) The real part of this is:

$$\text{Re } H_{so2} \psi = - \frac{e \hbar U}{4m^2 c^2} \underline{\sigma} \cdot \underline{B} \quad - (26)$$

$$= \frac{e^3 \hbar}{16\pi \epsilon_0 m^2 c^2 r} \underline{\sigma} \cdot \underline{B} \quad - (27)$$

Therefore:

$$\langle H_{so2} \rangle = \frac{e^3 \hbar}{16\pi \epsilon_0 m^2 c^2} \left\langle \frac{1}{r} \right\rangle \underline{\sigma} \cdot \underline{B}$$

where $\left\langle \frac{1}{r} \right\rangle = \int \psi^* \frac{1}{r} \psi d\tau \quad - (28)$

In general, $\langle 1/r \rangle$ must be worked out by computational quantum chemistry, leading to a new type of special ESR fine structure. In the H atom:

$$\begin{aligned} \langle U \rangle &= \int \psi^* U \psi d\tau \\ &= \frac{e^4}{16\pi^2 \epsilon_0^2 \hbar^2 c^2 n^2} \end{aligned} \quad - (29)$$

So:

$$\langle H_{so2} \rangle_H = \frac{e \hbar}{4m^2 c^2} \left(\frac{e^4}{16\pi^2 \epsilon_0^2 \hbar^2 c^2} \right) \frac{\underline{\sigma} \cdot \underline{B}}{n^2} \quad - (30)$$