Fundamental theory of EPR
Quantum mechanics

8th EFEPR-school, Brno, 2019

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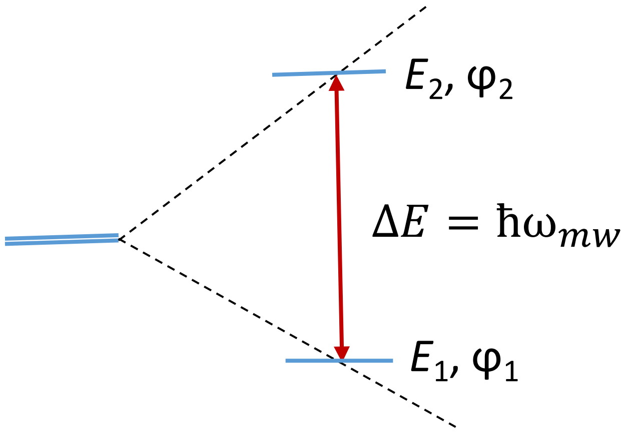
Leiden University

S=½ EPR spectrum

Energy-level diagram



1. Quantization of matter

$$i\hbar \frac{\partial \psi(\boldsymbol{r},t)}{\partial t} = \hat{H}(\boldsymbol{r},t)\,\psi(\boldsymbol{r},t)$$

Schrödinger equation

Erwin Schrödinger
Nobel prize in Physics 1933

In case $\hat{H}$ is NOT a function of time

$$\varphi_j(\boldsymbol{r})\exp\left(\frac{-iE_j t}{\hbar}\right)$$

Stationary state

$$\hat{H}(\boldsymbol{r})\;\varphi_j(\boldsymbol{r}) = E_j\,\varphi_j(\boldsymbol{r}).$$

Time-independent Schrödinger equation

1. Quantization of matter

$$i\hbar \frac{\partial \psi(\boldsymbol{r},t)}{\partial t} = \widehat{H}(\boldsymbol{r},t)\, \psi(\boldsymbol{r},t)$$

Schrödinger equation

In case $\widehat{H}$ is NOT a function of time

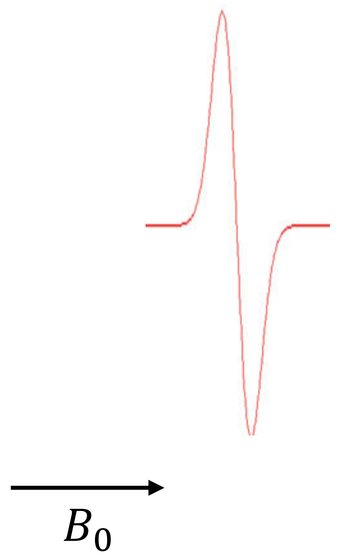
$$\psi(\boldsymbol{r},t) = \sum_{j=1}^{\infty} c_j\, \varphi_j(\boldsymbol{r}) \exp\left(\frac{-iE_j t}{\hbar}\right)$$

General solution: linear combination of stationary states

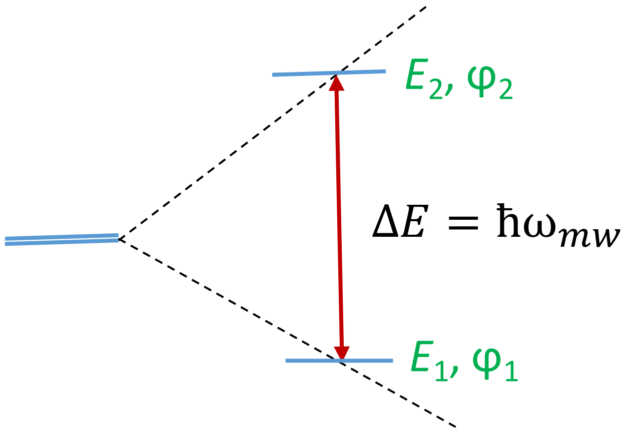
$$\widehat{H}(\boldsymbol{r})\ \varphi_j(\boldsymbol{r}) = E_j\, \varphi_j(\boldsymbol{r}).$$

Time-independent Schrödinger equation

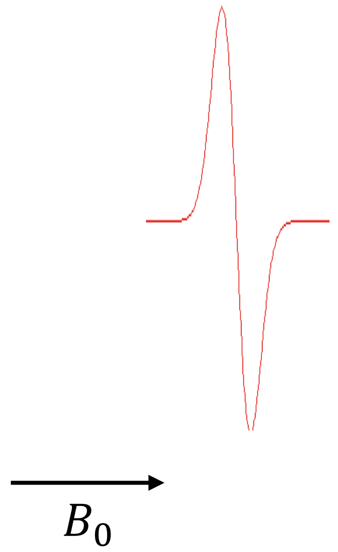
S=½ EPR spectrum



Energy-level diagram



S=½ EPR spectrum



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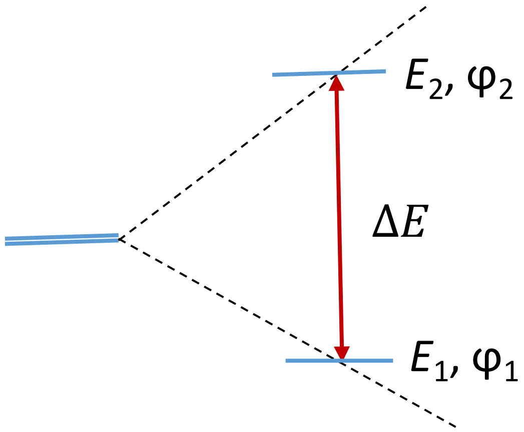
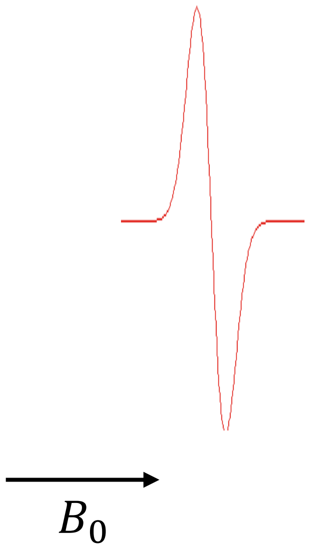


Stationary state

Transition?

Stationary state

S=½ EPR spectrum



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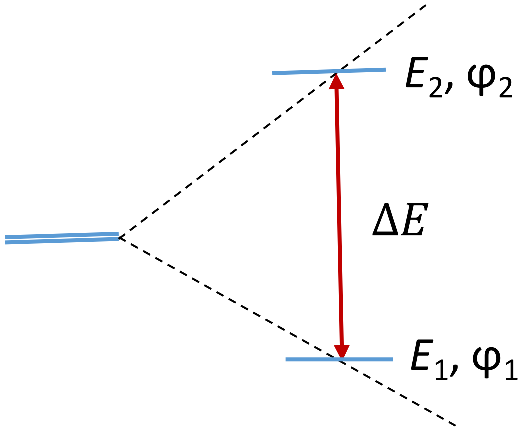

Stationary state

Transition?

Stationary state

2. Angular momentum

Classical physics: $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$

Quantum physics: Any vector operator $\hat{\boldsymbol{J}}$ with components $\widehat{J_x}, \widehat{J_y}, \widehat{J_z}$ such that the commutator $\widehat{J_x}\,\widehat{J_y} - \widehat{J_y}\,\widehat{J_x} \equiv [\widehat{J_x}, \widehat{J_y}] = i\,\widehat{J_z}$ (and similar for cyclic permutations of x, y, z), is associated with an angular momentum $\hbar J$.

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Pure mathematics: such a vector operator is characterized by states $|j\ m_j\rangle$ such that

$$\widehat{\boldsymbol{J}^2}\,|j\ m_j\rangle = j(j+1)|j\ m_j\rangle$$
$$\widehat{J_z}\,|j\ m_j\rangle = m_j|j\ m_j\rangle$$

$j = 0, 1/2, 1, 3/2, \ldots\ldots$
$m_j = j, j-1, j-2, \ldots\ldots\ldots, -j$.

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j= 0, 1/2, 1, 3/2, ...
$m_j = j, j-1, j-2, \ldots\ldots\ldots, -j$.

- *Orbital angular momentum* $\hbar\boldsymbol{L}$
- *Spin angular momentum* $\hbar\boldsymbol{S}$
- *Coupling of angular momenta* $\hbar\boldsymbol{J}_1$ *and* $\hbar\boldsymbol{J}_2$

Spin angular momentum $|s\ m_s\rangle$

Organic radical $s = ½$, $m_s = ½$, $-½$

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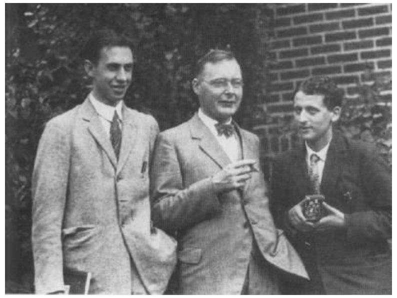
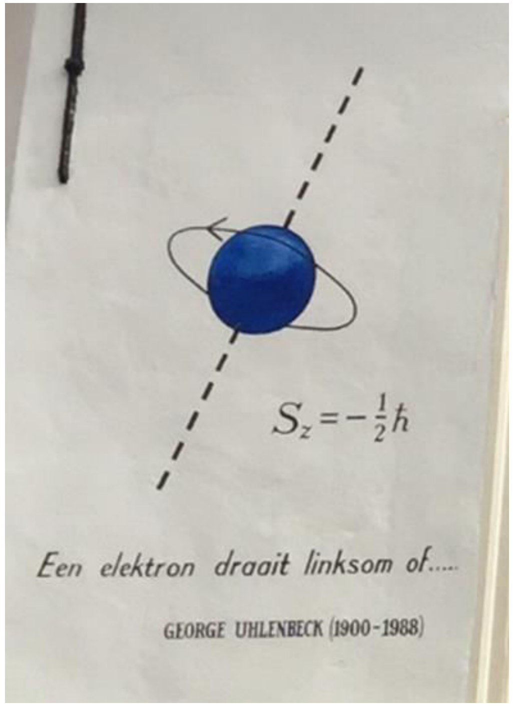


Uhlenbeck Goudsmit



Spin angular momentum $|s\ m_s\rangle$

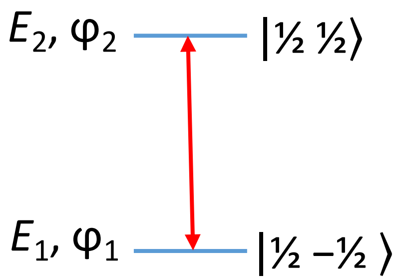
Organic radical $s = \frac{1}{2}$, $m_s = \frac{1}{2}$, $-\frac{1}{2}$

Fe (III), $(3d)^5$ configuration High spin $S = \frac{5}{2}$, $M_S = \frac{5}{2}$, $\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$, $-\frac{5}{2}$

Low spin $S = \frac{1}{2}$, $M_S = \frac{1}{2}$, $-\frac{1}{2}$

Spin angular momentum $|s\ m_s\rangle$

Organic radical s = ½ , m_s = ½ , -½



Fe (III), $(3d)^5$ configuration High spin S = 5/2 , M_S = 5/2 , 3/2 , ½ , -½ , -3/2 , -5/2

Low spin S = ½ , M_S = ½ , -½

3. Magnetic moment

Electron

orbital angular momentum $\hbar \boldsymbol{L}$ magnetic moment $\boldsymbol{\mu}_L = \frac{-e\hbar}{2m_e}\boldsymbol{L} \equiv -\beta_e \boldsymbol{L}$ *Bohr magneton*

Niels Bohr
Nobel prize in Physics 1922

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spin angular momentum $\hbar\boldsymbol{S}$ magnetic moment $\boldsymbol{\mu}_S = -g\,\beta_e\boldsymbol{S}$

Nuclei

spin angular momentum $\hbar\boldsymbol{I}$ magnetic moment $\boldsymbol{\mu}_I = g_N\beta_n\boldsymbol{I}$ *nuclear magneton*

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free electron $g = 2.00231930436082(52)$

$$g = 2\left(1 + \frac{\alpha}{2\pi} - 0.328\frac{\alpha^2}{\pi^2} + \cdots\right)$$

Nuclei

spin angular momentum $\hbar\boldsymbol{I}$ magnetic moment $\boldsymbol{\mu}_I = g_N \beta_n \boldsymbol{I}$ *nuclear magneton*

3. Magnetic moment

Magnetic moment in a magnetic field: $V = -\boldsymbol{\mu}.\boldsymbol{B}$

In quantum physics for the electron spin: $H = -\boldsymbol{\mu}_S.\boldsymbol{B} = g\beta_e\boldsymbol{S}.\boldsymbol{B}$

Electron

orbital angular momentum $\hbar\boldsymbol{L}$ — magnetic moment $\boldsymbol{\mu}_L = \frac{-e\hbar}{2m_e}\boldsymbol{L} \equiv -\beta_e\boldsymbol{L}$ — *Bohr magneton*

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4. Spin Hamiltonian

We know what we have to do: solve the time-independent Schrödinger equation $H\Psi_i = E_i\Psi_i$.

H and Ψ_i are functions of spatial and spin coordinates.

Instead of the full Hamiltonian we use a spin Hamiltonian, which only contains spin operators. The spatial coordinates have been absorbed in phenomenological parameters.

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spin operator

$$H_0 = \beta_e \widetilde{S} g B_0$$

g tensor

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Working with the spin Hamiltonian allows interpretation of the EPR spectrum without calculating the full wave function.

- Replace the Hamiltonian by the spin Hamiltonian.
- The spin Hamiltonian only works on the spin part of the wave function.
- Find the spin eigenfunctions and the corresponding eigenvalues.
- Interpret the EPR spectrum and determine the “tensors”.

- Interpret the tensors in terms of the electronic structure.

$Spin\ Hamiltonian \qquad H_0 = H_{eZ} + H_{zfs} + H_{hf} + H_{nZ} + H_{nq}.$

Spin Hamiltonian $H_0 = H_{eZ} + H_{zfs} + H_{hf} + H_{nZ} + H_{nq}$.

- *The electron Zeeman interaction* $H_{eZ} = \beta_e \tilde{\boldsymbol{S}} \boldsymbol{g} \, \boldsymbol{B}_0$.

Pieter Zeeman
Nobel prize in Physics 1902

g second rank tensor

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

in principal axes system

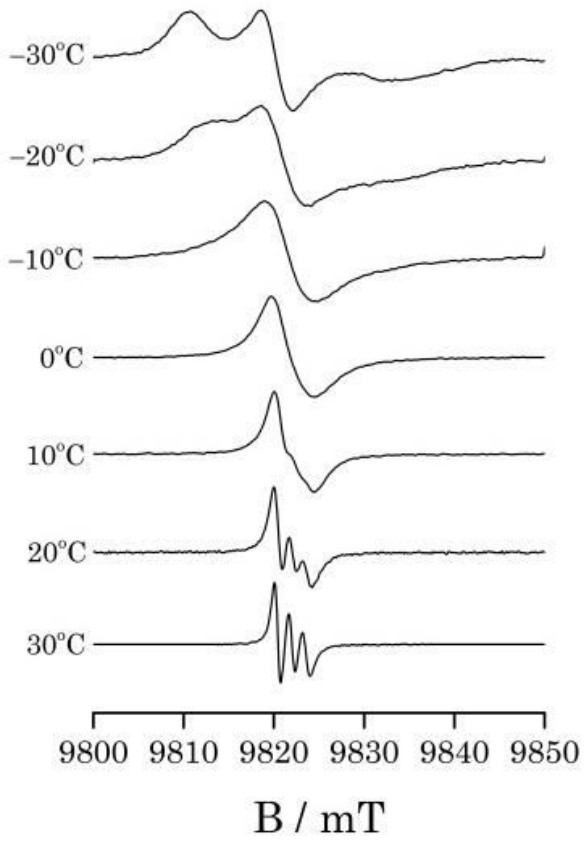
$$\begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix}$$

cubic symmetry $g_x = g_y = g_z$

axial symmetry $g_x = g_y \equiv g_\perp$ *and* $g_z \equiv g_\parallel$

S = ½   Spin label TEMPONE in water/glycerol (50/50 % vol)

EPR spectra
at 275 GHz



- *The zero-field splitting* $H_{zfs} = \tilde{\boldsymbol{S}}\,\boldsymbol{D}\,\boldsymbol{S}$. $S > 1/2$

D second rank tensor
in principal axes system

$$\begin{pmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{pmatrix}$$

When taken traceless

$$H_{zfs} = D\left[{S_z}^2 - \frac{1}{3}S(S+1)\right)\Big] + E({S_x}^2 - {S_y}^2\Big)$$

$$D \equiv 3\,D_z/2 \qquad E \equiv (D_x - D_y)$$

cubic symmetry $D = E = 0$
axial symmetry $D \neq 0, E = 0$
lower symmetry $D \neq E \neq 0$

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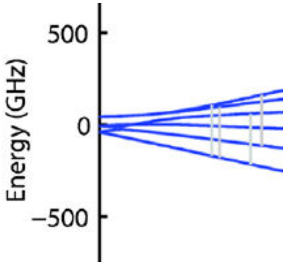
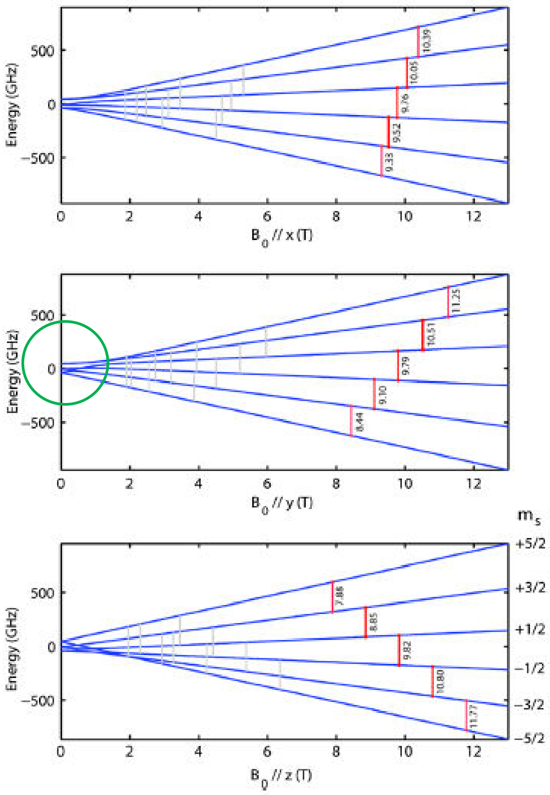
$$H_{zfs} = \frac{\mu_0}{4\pi} g^2 \beta_e^2 \left\{\frac{s_1.\,s_2}{r^3} - \frac{3(s_1.\,r)(s_2.\,r)}{r^5}\right\}$$

Human serum transferrin
high-spin Fe(III)
S = 5/2





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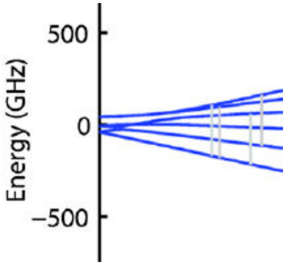

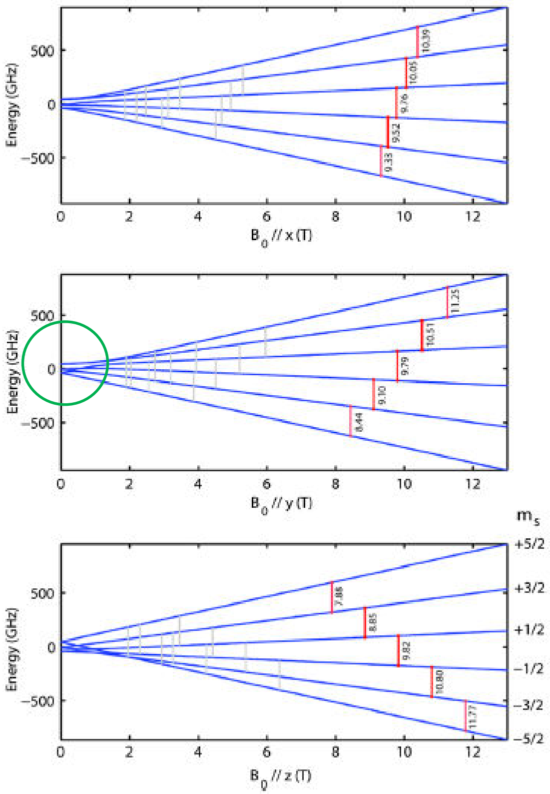

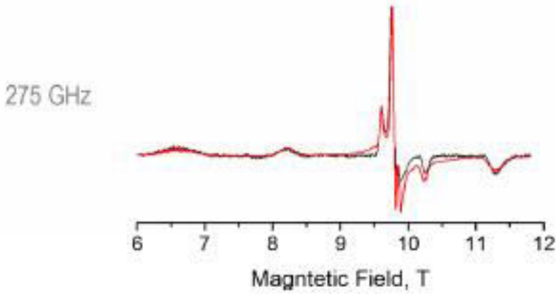

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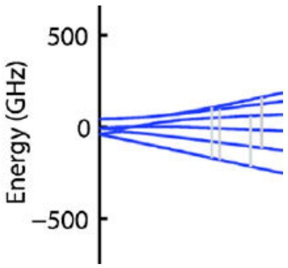
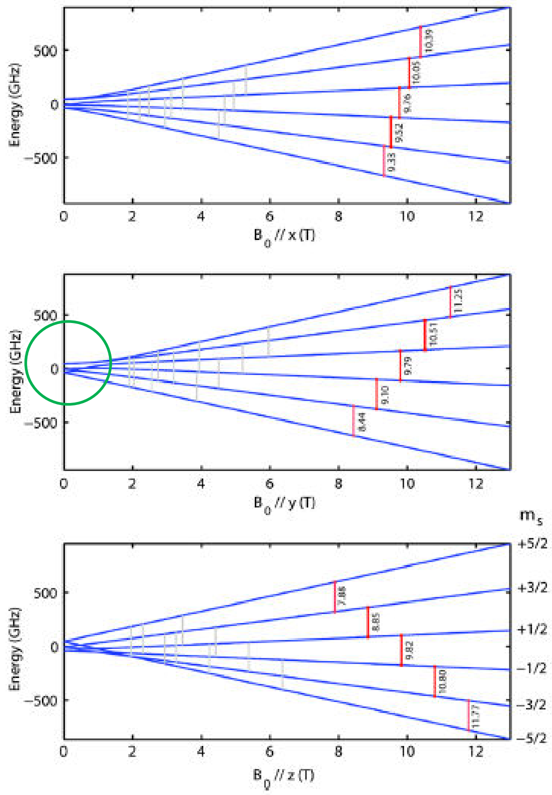
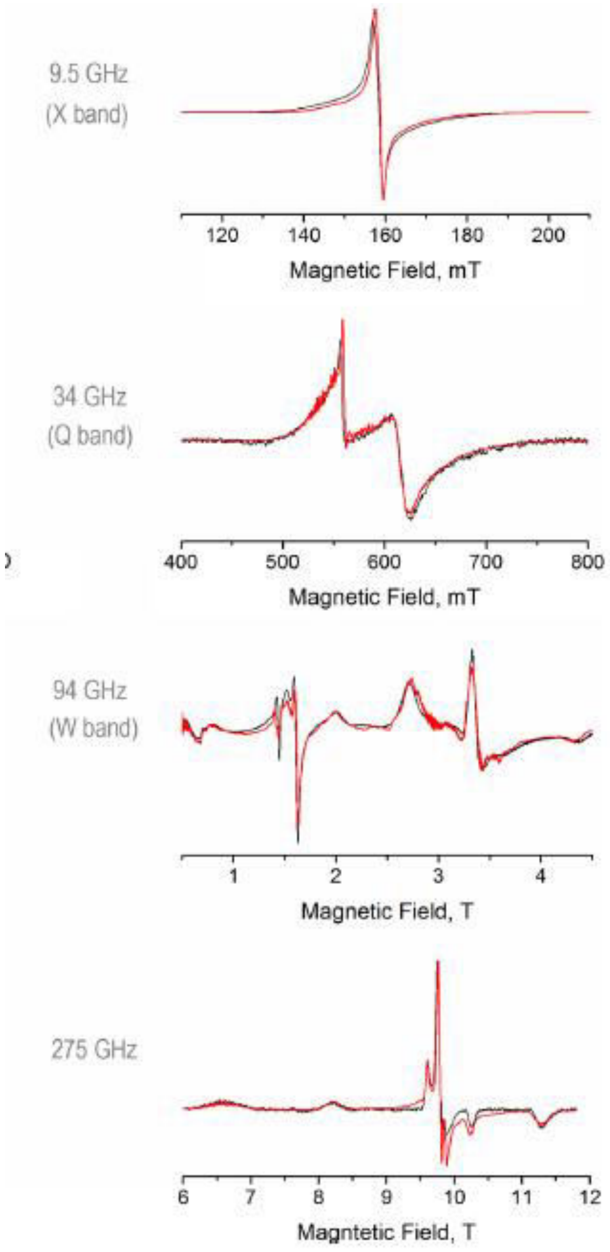






- *The hyperfine coupling* $H_{hf} = \sum_k \tilde{\boldsymbol{S}} \boldsymbol{A}_k \boldsymbol{I}_k.$

$$\boldsymbol{A} = a_{iso}\boldsymbol{1} + \boldsymbol{T}.$$

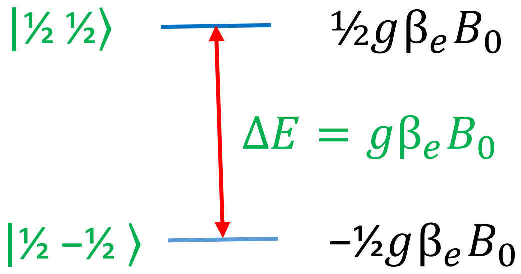
- *The nuclear Zeeman interaction* $H_{nZ} = -\beta_n \sum_k g_k \tilde{\boldsymbol{I}}_k \boldsymbol{B}_0.$

- *The nuclear quadrupole interaction* $H_{nq} = \tilde{\boldsymbol{I}} \boldsymbol{P} \boldsymbol{I}.$ $I \geq 1$

5. EPR transitions

Electron spin in a magnetic field $\mathbf{B}_0 = (0, 0, B_0)$

$$\widehat{H_0}|s\ m_s\rangle = g\beta_e B_0 \widehat{\boldsymbol{S}_z}|s\ m_s\rangle = g\beta_e B_0 m_s|s\ m_s\rangle$$



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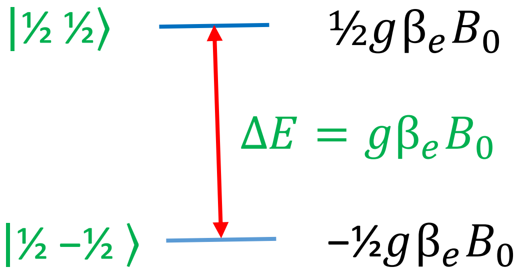


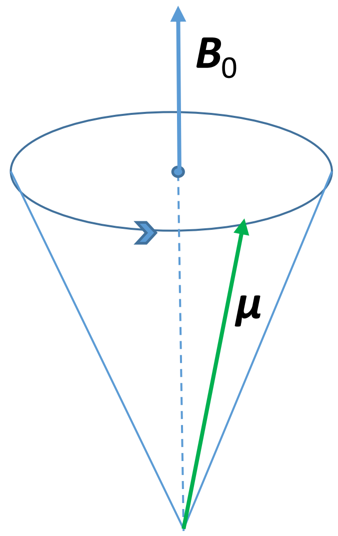
Transition?

$$H_1(t) = \beta_e \tilde{S} g B_1(t)$$

probability

$$|\langle ½\ ½|H_1|½\ {-½}\rangle|^2\ \delta(\Delta E - \hbar\omega_{mw})$$

6. Equation of motion



classical mechanics

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times \gamma \boldsymbol{B}_0$$

precession of $\boldsymbol{\mu}$ around $\boldsymbol{B}_0$ with angular frequency

$$\omega_0 = \gamma B_0$$

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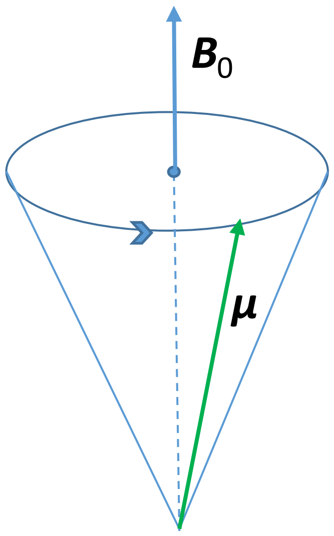

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in reference frame that rotates with angular frequency $\boldsymbol{\Omega}$:

$$\frac{\delta\boldsymbol{\mu}}{\delta t} = \boldsymbol{\mu} \times \gamma \boldsymbol{B}_{eff}$$

$$\boldsymbol{B}_{eff} = \boldsymbol{B}_0 + \frac{\boldsymbol{\Omega}}{\gamma}$$

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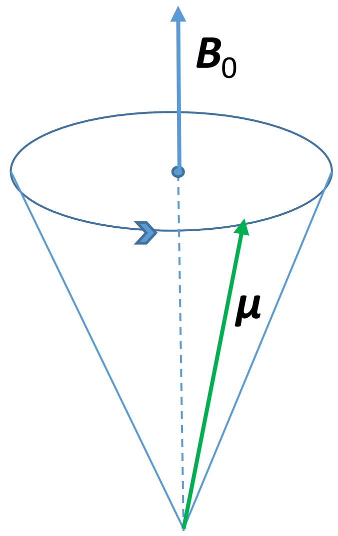

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quantum mechanics

this description applies to

- the expectation value of $\boldsymbol{\mu}$
- the magnetization $\boldsymbol{M}$ of an ensemble of spins

EPR experiment

$$\boldsymbol{B}(t) = \boldsymbol{B}_0 + \boldsymbol{B}_1(t)$$

$$\frac{d\boldsymbol{M}}{dt} = \boldsymbol{M} \times (-g\,\beta_e/\hbar)[\boldsymbol{B}_0 + \boldsymbol{B}_1(t)]$$

$$\boldsymbol{B}_1(t) = 2B_1 \cos(\omega_{mw} t)\ \boldsymbol{e}_x$$

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In rotating frame,
angular frequency ω_{mw} about z-axis

$$\frac{\delta\boldsymbol{M}}{\delta t} = \boldsymbol{M} \times \left(\frac{-g\beta_e}{\hbar}\right)\boldsymbol{B}_{eff}$$

precession about $\boldsymbol{B}_{eff}$

$$\boldsymbol{B}_{eff} = \left(B_0 - \frac{\hbar\omega_{mw}}{g\beta_e}\right)\boldsymbol{e}'_z + B_1\boldsymbol{e}'_x$$

$\boldsymbol{B}_{eff}$ almost parallel z'- axis,
even close to resonance

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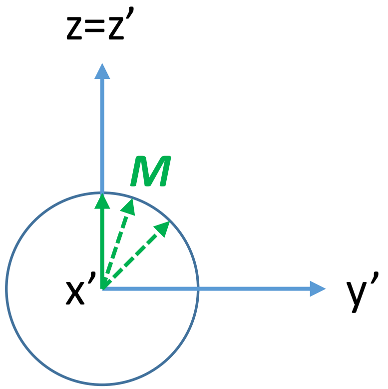
At resonance $\boldsymbol{B}_{eff} = B_1\boldsymbol{e}'_x$, which implies a precession of $\boldsymbol{M}$ about $\boldsymbol{e}'_x$, in the $(\boldsymbol{e}'_y - \boldsymbol{e}'_z)$ - plane,
with the so-called Rabi frequency

$$\omega_1 = \left(\frac{g\beta_e}{\hbar}\right)B_1\ .$$



Ensemble of spins in thermal equilibrium, switching on $\boldsymbol{B}_1(t)$ at $t = 0$:

$$M_z(t) = M_0 \cos\omega_1 t.$$

After a short time τ the magnetization ***M*** has turned over an angle $\omega_1\tau$ in the rotating frame.

After rotation over 90 degrees (π/2-pulse) $M_z = 0$,
after rotation over 180 degrees (π-pulse) $M_z = -M_0$.

7. Density matrix formalism

S = ½ $|½\ ½\rangle \equiv |1\rangle$ $|½\ {-½}\rangle \equiv |2\rangle$

Arbitrary spin state $|\chi\rangle = c_1|1\rangle + c_2|2\rangle$ $\boldsymbol{\chi} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$

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Arbitrary spin state $|\chi\rangle = c_1|1\rangle + c_2|2\rangle$ $\boldsymbol{\chi} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$ $\langle\chi| = \langle 1|c_1^* + \langle 2|c_2^*$ $\boldsymbol{\chi}^\dagger = (c_1^*\ c_2^*)$

7. Density matrix formalism

ket-vector

$\langle \quad | \quad \rangle$

bra(c)ket

bra-vector

S = ½ $\quad |½\ ½\rangle \equiv |1\rangle \qquad |½\ {-½}\rangle \equiv |2\rangle$

Arbitrary spin state $|\chi\rangle = c_1|1\rangle + c_2|2\rangle \qquad \boldsymbol{\chi} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad \langle\chi| = \langle 1|c_1^* + \langle 2|c_2^* \qquad \chi^\dagger = (c_1^*\ c_2^*)$

Paul Dirac
Nobel prize in Physics 1933

7. Density matrix formalism

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$$< A > = \boldsymbol{\rho}_{11}\mathbf{A}_{11} + \boldsymbol{\rho}_{21}\mathbf{A}_{12} + \boldsymbol{\rho}_{12}\mathbf{A}_{21} + \boldsymbol{\rho}_{22}\mathbf{A}_{22} = \sum_j \sum_k \boldsymbol{\rho}_{jk}\mathbf{A}_{kj} = \sum_j (\boldsymbol{\rho}\mathbf{A})_{jj} = \mathrm{Tr}(\boldsymbol{\rho}\mathbf{A})$$

7. Density matrix formalism

$S = 1/2$ $\quad |\tfrac{1}{2}\,\tfrac{1}{2}\rangle \equiv |1\rangle$ $\quad |\tfrac{1}{2}\,-\tfrac{1}{2}\rangle \equiv |2\rangle$

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$$\boldsymbol{\rho} = \begin{pmatrix} c_1 c_1^* & c_1 c_2^* \\ c_2 c_1^* & c_2 c_2^* \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} (c_1^* c_2^*) = \boldsymbol{\chi}\,\boldsymbol{\chi}^\dagger \qquad \rho = |\chi\rangle\,\langle\chi| \quad \text{density operator}$$

Evolution of the spin state $|\chi\rangle$ under the Hamiltonian H:

Schrödinger equation $i\hbar \frac{\partial}{\partial t}|\chi\rangle = H|\chi\rangle$

in matrix form $i\hbar\, \dot{\boldsymbol{\chi}} = \mathbf{H}\, \boldsymbol{\chi}$

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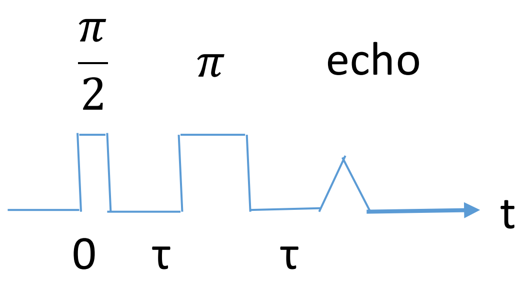

$$\rho(2\tau) = \exp\left(-\tfrac{i}{\hbar}H\tau\right)\exp\left(-i\pi S_x\right)\exp\left(-\tfrac{i}{\hbar}H\tau\right)\exp\left(-i\tfrac{\pi}{2}S_x\right)\rho(0)\exp\left(+i\tfrac{\pi}{2}S_x\right)\exp\left(+\tfrac{i}{\hbar}H\tau\right)\exp\left(+i\pi S_x\right)\exp\left(+\tfrac{i}{\hbar}H\tau\right)$$

So far for the introduction to the

8th BRNO EFEPR SCHOOL

18–25/11/2019

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BRNO, Czech Republic

of the European Federation of EPR groups on Advanced EPR

Tutorials

1. Angular momentum.
2. Coupling of two spin-½ systems: a biradical.
3. Spin Hamiltonian.
4. The EPR spectrum of a nitroxide radical at 9.5 and 275 GHz.
5. High-spin Co(III).
6. Density matrix.
7. A two-spin system and the evolution of the density matrix: electron-spin-echo spectroscopy of radical pairs.