Lecture 26

Thursday, January 27, 2022 2:41 PM

Blundell –

Abragam and Bleaney – EPR in transition metal ions

ESR Studies of Cu, Ag, and Au Atoms Isolated in Rare-Gas Matrices

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(Received 1 April 1971)

TABLE I. Cu atom in rare-gas matrix at 4°K.

Matrix	$A(^{63}Cu)$ [a] in MHz	g	$(\Delta A/A_0)\times 100$ [b]	Δg
Ne	6000±10	1.999±0.001	+2	−0.003
Ar	6151±1	1.9994±0.0002	+4.8	−0.0029
Kr	6043±1	1.9955±0.0002	+3.0	−0.0068
Xe	5895±3	1.9942±0.0006	+0.5	−0.0081
Free atom	5867[b]			

[a] For ^{65}Cu, we obtained $A(^{65}Cu) = (1.0709\pm0.0001)\ A(^{63}Cu)$ for all matrices.

[b] $A_0 = 5867$ MHz obtained from an atom beam experiment, Ref. 11.

6 GHz

d-shell

↑↓ ↑↓ ↑↓ ↑↓ ↑↓

s-shell

↑

The Isotropic Hyperfine Interaction[1]

by B. R. McGarvey

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York
(Received September 27, 1966)

↑↓ ↑↓ ↑↓ ↑↓ ↑

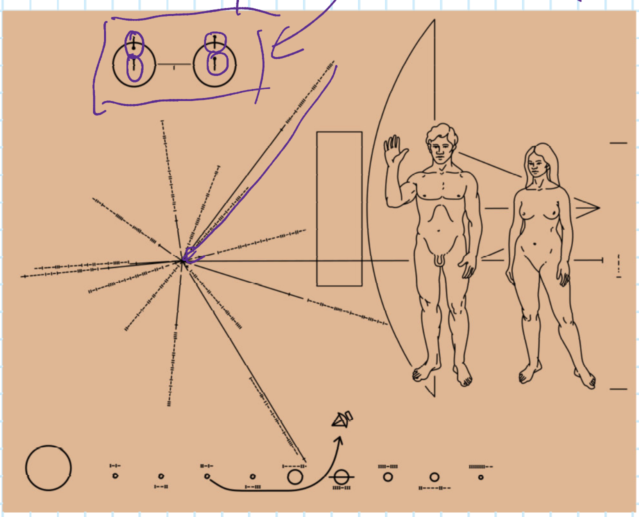
↑↓

Host lattice	$g_{\parallel}$	$g_{\perp}$ [bb]	$10^4 A$, cm^{-1}	$10^4 B$,[bb] cm^{-1}
$Cu^{2+}(3d^9)$				
MgO	2.190		(−)19	
CaO	2.221		(−)21.5	
$Mg_3Bi_2(NO_3)_{12}\cdot 24H_2O$ (90°K)	2.219		(−)27	
$Mg_3Bi_2(NO_3)_{12}\cdot 24H_2O$ (20°K)	2.454	2.096	(−)110	(+)17
$Mg_3La_2(NO_3)_{12}\cdot 24H_2O$ (90°K)	2.219		(−)29	
$Mg_3La_2(NO_3)_{12}\cdot 24H_2O$ (20°K)	2.470	2.097	−113	+15.6
TiO_2	2.344	2.099	−88	−23
$Pd[(CH_3CO)_2CH]_2$	2.2661	2.0535	−160	−19.5
$Ni\{OC_6H_4CHNH\}_2$	2.2004	2.0448	−185	−21
$[(C_4H_9)_4N]_2Ni[S_2C_2(CN)_2]_2$	2.086	2.024	(−)162	(−)39
$Zn[(C_2H_5)_2NCS_2]_2$	2.1085	2.023	(−)142.4	(−)22.4
H_2Pc	2.179	2.050	(−)202	(−)19
ZnPc	2.162	2.047	(−)215	(−)28
$Cu(OC_6H_4CHNOH)_2$	2.171	2.020	(−)183	(−)41
$Cu(OC_9H_6N)_2$	2.172	2.042	(−)162	(−)25
$Zn(OC_9H_6N)_2\cdot 2H_2O$	2.287	2.066	(−)171	(−)30
$\{Zn(phen)_3\}(NO_3)_2$	2.273	2.062	(−)171	(−)36
$Cd[C_5H_5N]_4S_2O_8$	2.264	2.042	(−)169	(−)14.7
$Cu\{[(CH_3)_2CH]_2NCS_2\}_2$	2.087	2.023	−154	−35
$[(C_2H_5)_4N]_2Cu(S_2C_2O_2)_2$	2.083	2.024	(−)171	(−)48
$Cu(C_5H_5N)_6(NO_3)_2$	2.25	2.05	(−)199	(−)14
Cu etioporphyrin	2.169	2.062	(−)188	(−)39
$CdCl_2$	2.339	2.070	(−)113	0
Cs_2ZnCl_4	2.446	2.092	(−)25	(−)49

100 MHz

Pioneers Plaque

21 cm-line (radio-astronomic)



(1) Fermi-contact interaction (isotropic)

(2) magnetic dipole interaction

(1) comments

- isotropic, because s-orbitals are isotropic
- Can be large or small, strongly dependent on the population of the s-orbital

(1) + (2)

↳ Both interactions allow to probe your electronic, magnetic and chemical structure + environment [solids, molecules + atoms]
[nuclear spin is a spy inside the atom]

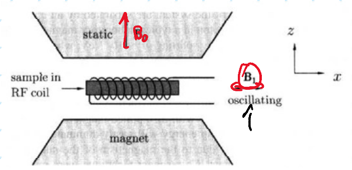
↳ Free atoms: very precise measure and used for atomic clocks

7.1. Magnetic Resonance Techniques [Experimental Probes of Magnetism]

NMR
Nuclear Magnetic Resonance
↓
MRI
Magnetic Resonance Imaging

ESR (EPR)
Electron Spin Resonance (Paramagnetic)

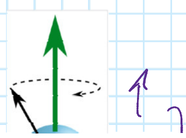
NMR

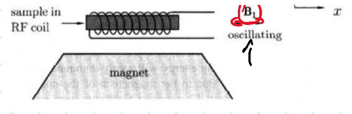


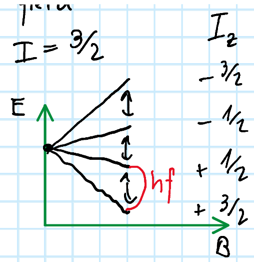
Nuclear spins in an external magnetic field

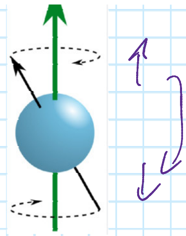
$I = 3/2$ $\quad I_z$

$-3/2$









$$E = -g_N \cdot \mu_N \cdot m_I \cdot B$$

$$\Delta E = h \cdot f = g_N \cdot \mu_N \cdot B \cdot \Delta m_I$$

Idea: excite the transition between two energy levels by a radiowave of the same frequency f

$\Rightarrow$ apply an oscillating B-field B_1 perpendicular to B_0

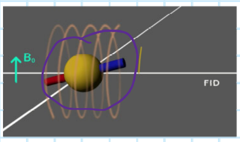
$$B_1 \propto I_x \rightarrow \langle m_I' | I_x | m_I \rangle > 0 \quad \text{if} \quad m_I' = m_I \pm 1$$

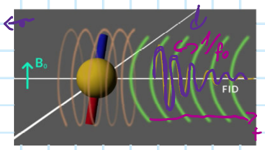
$$\boxed{\Rightarrow \text{ selection rules } \Delta m_I = \pm 1}$$

1. $I_x \propto \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

$$\sigma_x \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

2. rotating @ the speed of f (larmor precession)





T_1 - time: spin-lattice relaxation time

Bloch - Equations

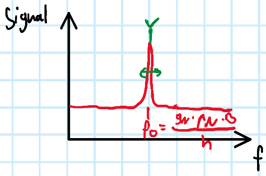
$$\frac{dM_x}{dt} = \gamma \left(\vec{M} \times \vec{B} \right)_x - \frac{M_x}{T_2}$$ spin-spin-relaxation

$$\frac{dM_y}{dt} = \gamma \left(\vec{M} \times \vec{B} \right)_y - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = \gamma \left(\vec{M} \times \vec{B} \right)_z - \frac{M_z - M_0}{T_1}$$ spin-lattice relaxation

Detection via free induction decay (FID)

$\Downarrow$ fourier transformation



1. example:

hydrogen ($I = 1/2$) in a field of 1T

$$f = 85 \text{ MHz}$$

$$hf = \Delta E = k_B T \rightarrow T = 4 \text{ mK}$$ very very hard

$f = 85\ \text{MHz}$

$hf = \Delta E = k_B T \rightarrow \boxed{T = 4\ \text{mK}}$ very very hard

⇒ at room temperature only a tiny fraction of nuclear spins is changed from its equilibrium

↳ abundant

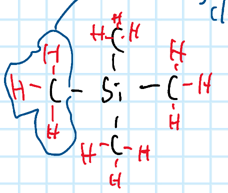
↳ resonance technique

Chemical sensitivity

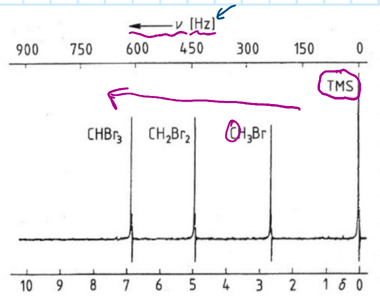
Principle: Different molecules show different f_0 for the same element (often H)

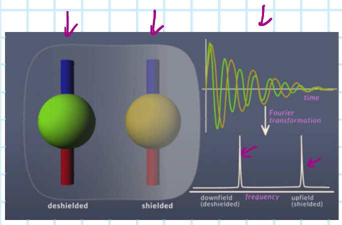
shielding e^- cloud (diamagnetism)

H



Tetramethylsilane (TMS) $Si(CH_3)_4$

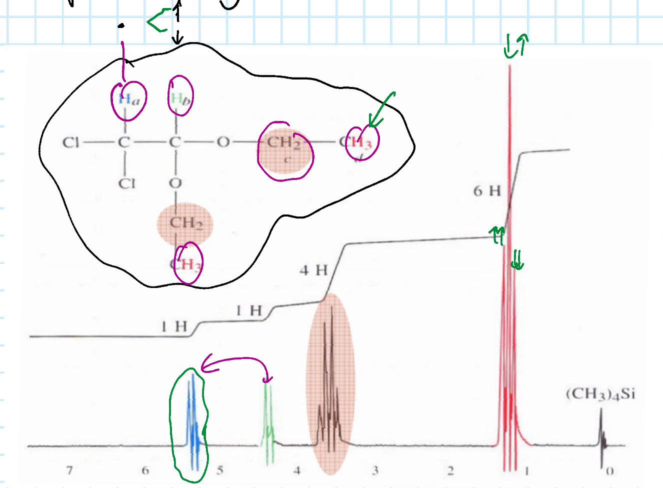




Chemical shift

$$\delta = \frac{\overbrace{(f - f_{ref})}^{Hz}}{\underbrace{f_{ref}}_{MHz}} \quad \text{in ppm}$$

spin-spin coupling



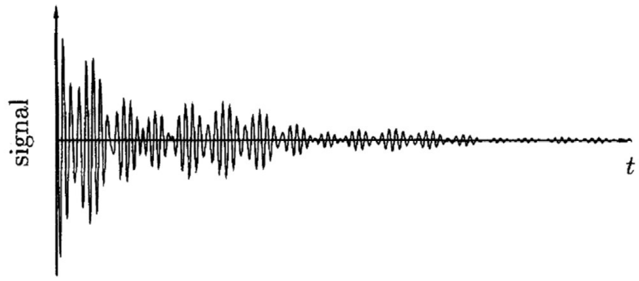
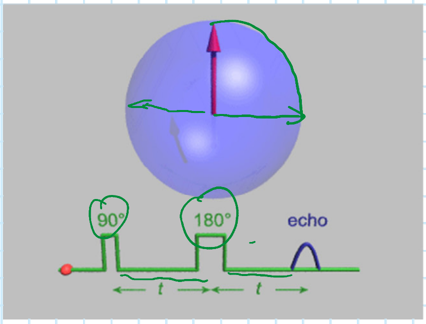


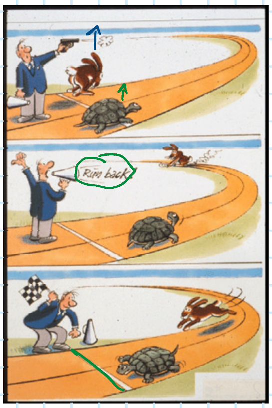
Fig. 3.12 A simulated free induction decay signal. The oscillations die away with time due to spin–spin relaxation (T_2 processes). The data show an interference pattern which results from three inequivalent nuclei, each of which experiences a slightly different magnetic field because of their different sites within a crystal.

Spin Dynamics

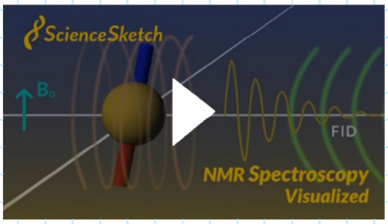
- Interaction with the environment
- inhomogeneous broadening (magnet)
- Can be prolonged by pulse-techniques

Hahn-Echo





[NMR spectroscopy]



[11.04 Chemical Shift]