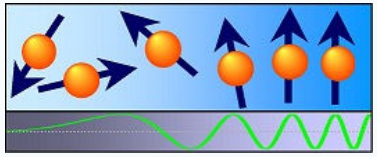
Experimental Physics EP3

Atoms and Molecules

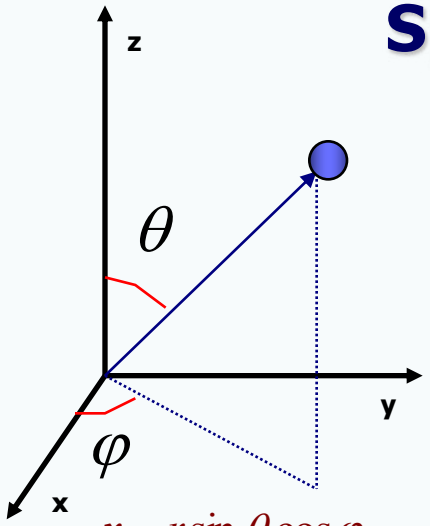
– Hydrogen atom –

Radial density distribution, energy levels, interaction with magnetic field



https://bloch.physgeo.uni-leipzig.de/amr/

Spherically symmetric potential



$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + U(\mathbf{r})\Psi$$

$$E\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\psi$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + (U-E)\psi = 0$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+$$
$$+\frac{2m}{\hbar^2}(E-U)\psi = 0$$

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

$$\left| \times r^2\sin^2\theta \right.$$

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial^2\psi}{\partial\varphi^2}+\frac{2m}{\hbar^2}r^2\sin^2\theta(E-U)\psi = 0$$

$$\frac{\sin^2\theta}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{2m}{\hbar^2}r^2\sin^2\theta(E-U) = -\frac{1}{\Phi(\varphi)}\frac{\partial^2\Phi(\varphi)}{\partial\varphi^2} = \mathbf{C_1}$$

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2m}{\hbar^2}r^2(E-U) = \frac{C_1}{\sin^2\theta}-\frac{1}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) = \mathbf{C_2}$$

Radial part of the wave function

$$\Psi(r,\theta,\varphi) = R(r)\mathrm{Y}_l^m(\theta,\varphi) = R(r)P_l^m(\cos\theta)\Phi(\varphi) \qquad \frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2m}{\hbar^2}r^2\left(E-U\right)=C_2=l(l+1)$$

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2m}{\hbar^2}r^2\left(E-\left[U+\frac{l(l+1)\hbar^2}{2mr^2}\right]\right)=0$$

Still spherically-symmetric field!
The angular part of WF remains uncahged.

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\left(-\beta^2r^2+qr-l(l+1)\right)R(r)=0 \qquad R(r)=\frac{u(r)}{r}e^{-\beta r}$$

$$U=-\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\frac{d^2u}{dr^2}-2\beta\frac{du}{dr}+\left(\frac{q}{r}-\frac{l(l+1)}{r^2}\right)u=0 \qquad u(r)=\sum_{k=\gamma}^{n}a_k r^k$$

$$\beta^2\equiv-\frac{2mE}{\hbar^2}$$

$$q\equiv\frac{mZe^2}{2\pi\varepsilon_0\hbar^2}$$

$$\sum_{k=\gamma}^{n}\left(a_k k(k-1)r^{k-2}-2\beta a_k k r^{k-1}+q a_k r^{k-1}-l(l+1)a_k r^{k-2}\right)=0$$

$k=\gamma$: $\gamma(\gamma-1)-l(l+1)=0$ ~~$\gamma=-l$~~ $\gamma=l+1$

$k=n$: $2\beta n-q=0$

$$E=-\frac{q^2\hbar^2}{4\cdot 2m}\frac{1}{n^2}=-\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2}$$

Function of n only!
Each level is n^2 times degenerate.

The Bohr's models

$$E_n=-\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{m}{2\hbar^2n^2}$$

Normalized radial wave function

$$R(r) = \frac{u(r)}{r} e^{-\beta r} \qquad u(r) = \sum_{k=l+1}^{n} a_k r^k \qquad R_{n,l}(r) = \sum_{k=l+1}^{n} a_k r^{k-1} \exp\left\{-\frac{Zr}{a_0 n}\right\}$$

$$R_{1,0} = 2Ne^{-Zr/a_0}$$

$$R_{2,0} = 2N\left(1 - \frac{Zr}{2a_0}\right)e^{-Zr/2a_0}$$

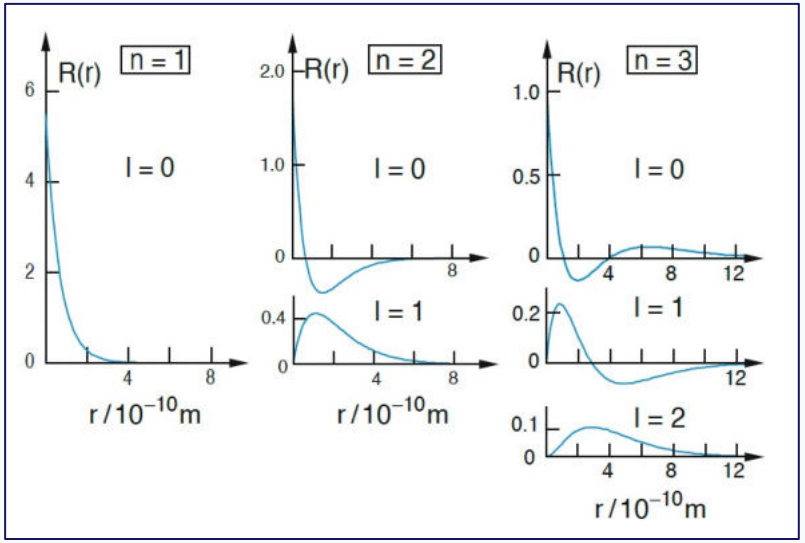
$$R_{2,1} = \frac{1}{\sqrt{3}} N \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{3,0} = 2N\left(1 - \frac{2Zr}{3a_0} + \left(\frac{2(Zr)^2}{27a_0^2}\right)\right)e^{-Zr/3a_0}$$

$$R_{3,1} = \frac{4\sqrt{2}}{3} N \left(\frac{Zr}{a_0}\right)\left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{3,2} = \frac{2\sqrt{2}}{27\sqrt{5}} N \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

$$l < n; \quad -l \le m \le l$$



$$\Psi(r, \theta, \varphi) = R_{n,l}(r) Y_l^m(\theta, \varphi)$$

$$\beta^2 \equiv -\frac{2mE}{\hbar^2} = \frac{Z^2}{a_0^2 n^2} \qquad a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} \qquad N = \left(\frac{Z}{na_0}\right)^{\frac{3}{2}}$$

l =	0	1	2	3	4
label	s	p	d	f	g

Spherically symmetric potential (m≠0)

$$\frac{d}{d\xi}\left(\left(1-\xi^2\right)\frac{d\Theta}{d\xi}\right)+\left(C_2-\frac{m^2}{1-\xi^2}\right)\Theta=0$$

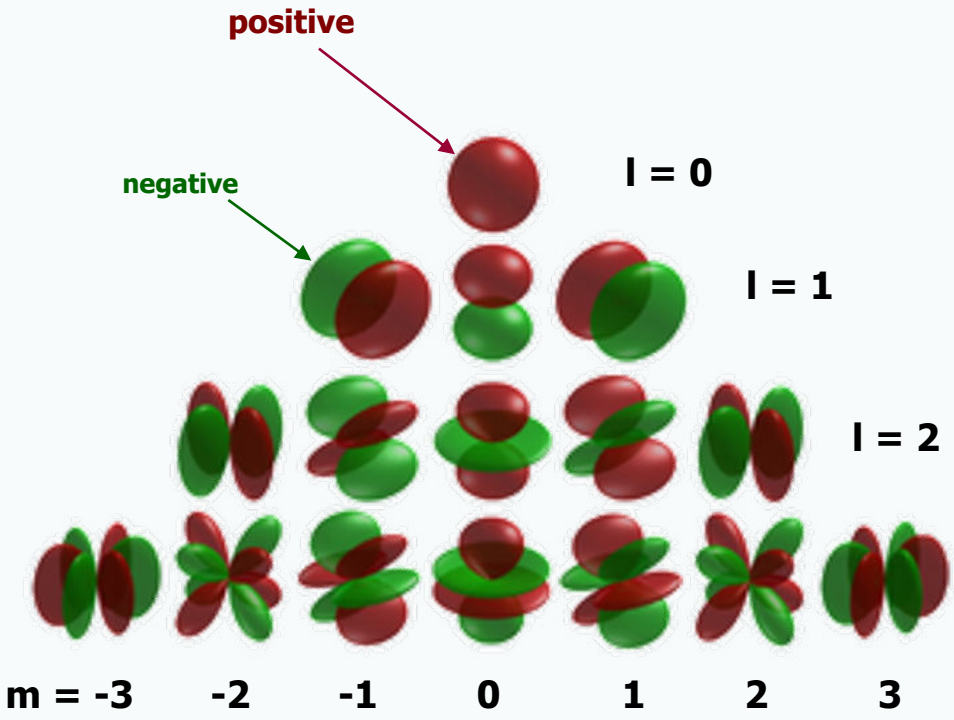
$$\Theta=P_l^m(\xi)=A\left(1-\xi^2\right)^{\left|\frac{m}{2}\right|}\frac{d^{|m|}}{d\xi^{|m|}}P_l(\xi)$$

$$Y_l^m(\theta,\varphi)=P_l^m(\cos\theta)\Phi(\varphi)$$

Otherwise you cannot define the differential

$$-l<m<l$$

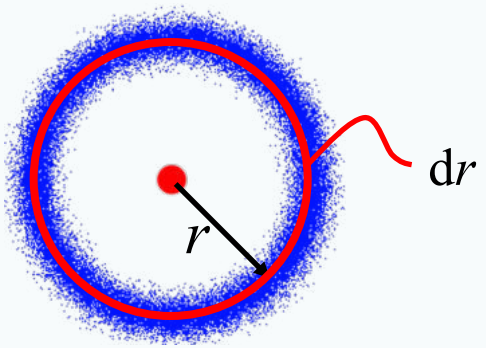
l	m	Y_l^m
0	0	$\frac{1}{2\sqrt{\pi}}$
1	±1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\vartheta\, e^{\pm i\varphi}$
	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\vartheta$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\vartheta\, e^{\pm 2i\varphi}$
	±1	$\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\vartheta\,\sin\vartheta\, e^{\pm i\varphi}$
	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(2\cos^2\vartheta-\sin^2\vartheta)$
3	±3	$\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\vartheta\, e^{\pm 3i\varphi}$
	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\cos\vartheta\,\sin^2\vartheta\, e^{\pm 2i\varphi}$
	±1	$\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\vartheta\,(5\cos^2\vartheta-1)\, e^{\pm i\varphi}$
	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\vartheta-3\cos\vartheta)$

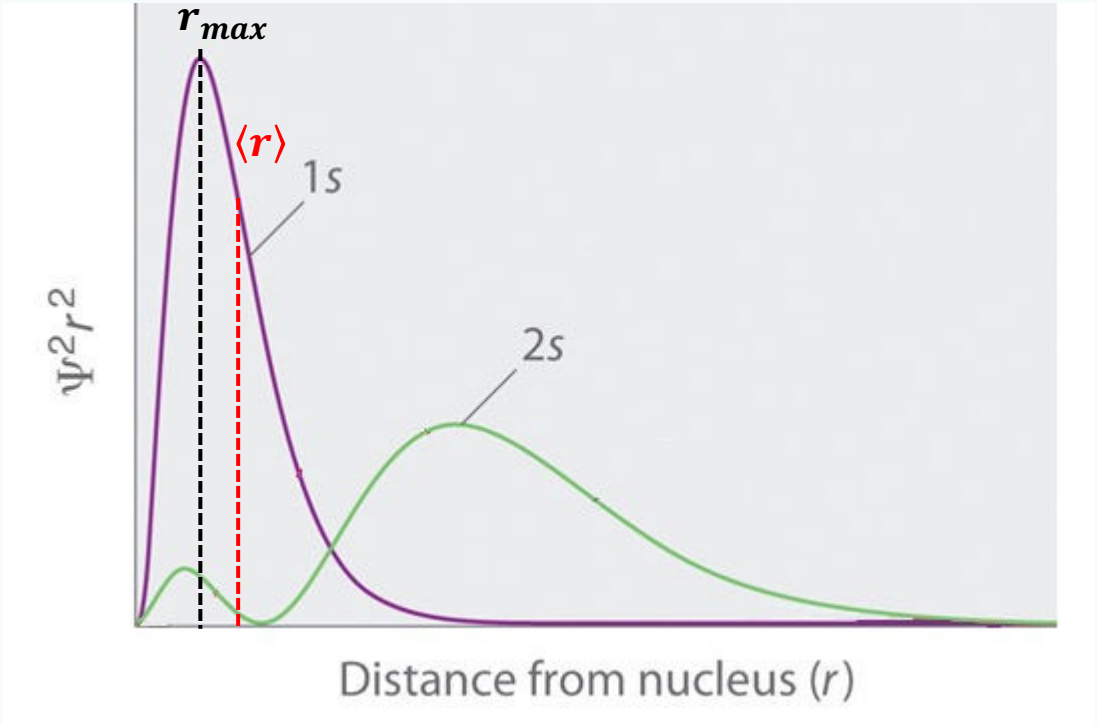


Radial density distribution

$$P(r)\mathrm{d}r = \int_{\vartheta=0}^{\pi}\int_{\varphi=0}^{2\pi} |\psi(r,\vartheta,\varphi)|^2 r^2 \mathrm{d}r \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi$$

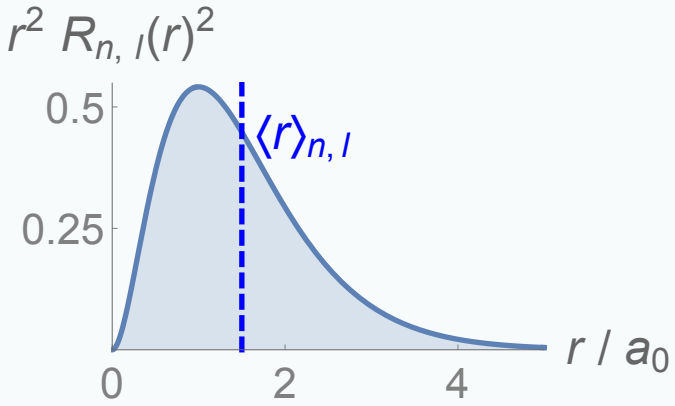
$$\boldsymbol{P_s(r)dr = r^2|R(r)|^2 dr}$$

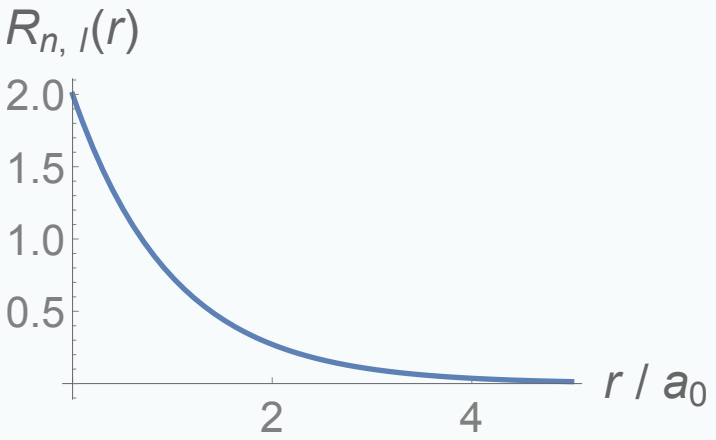




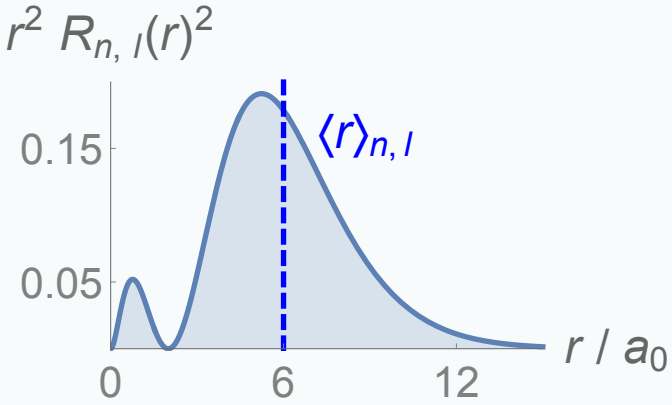
n	l	m	Eigenfunction $\psi_{n,l,m}(r,\vartheta,\varphi)$
1	0	0	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\vartheta$
2	1	±1	$\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\vartheta\, e^{\pm i\varphi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\cos\vartheta$
3	1	±1	$\frac{1}{\sqrt{81\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\sin\vartheta\, e^{\pm i\varphi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\vartheta-1)$
3	2	±1	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin\vartheta\cos\vartheta\, e^{\pm i\varphi}$
3	2	±2	$\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin^2\vartheta\, e^{\pm 2i\varphi}$

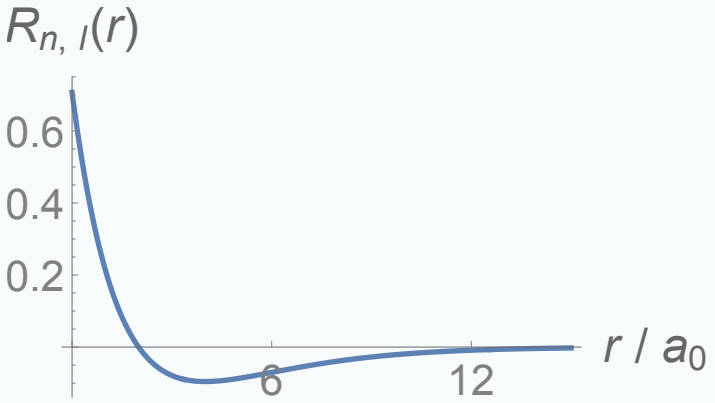
1s


$r^2\ R_{n,\,l}(r)^2$
0.5
0.25
$\langle r \rangle_{n,\,l}$
0
2
4
$r\ /\ a_0$

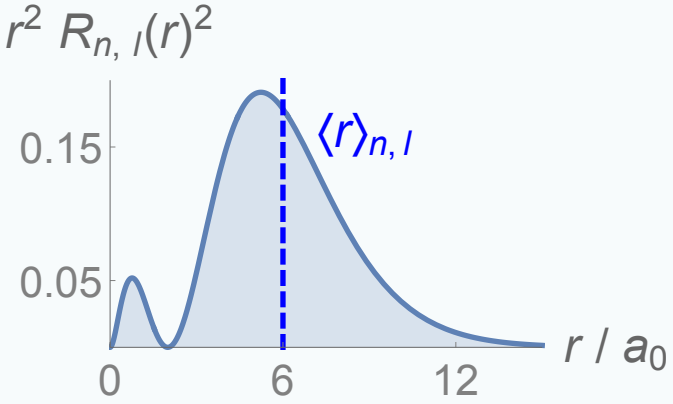

$R_{n,\,l}(r)$
2.0
1.5
1.0
0.5
2
4
$r\ /\ a_0$

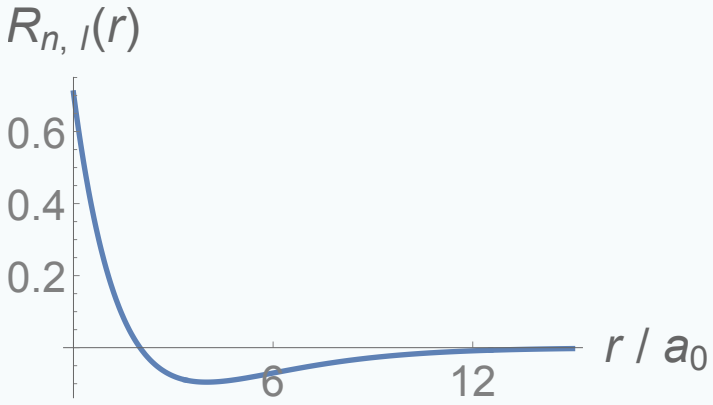
2s


$r^2\ R_{n,\,l}(r)^2$
0.15
0.05
$\langle r \rangle_{n,\,l}$
0
6
12
$r\ /\ a_0$

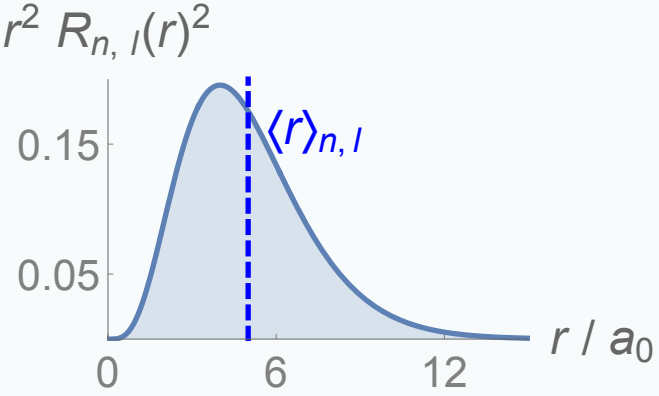

$R_{n,\,l}(r)$
0.6
0.4
0.2
6
12
$r\ /\ a_0$

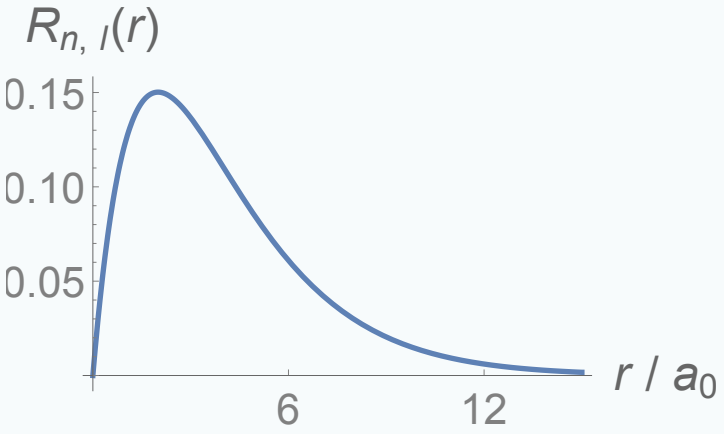
2s

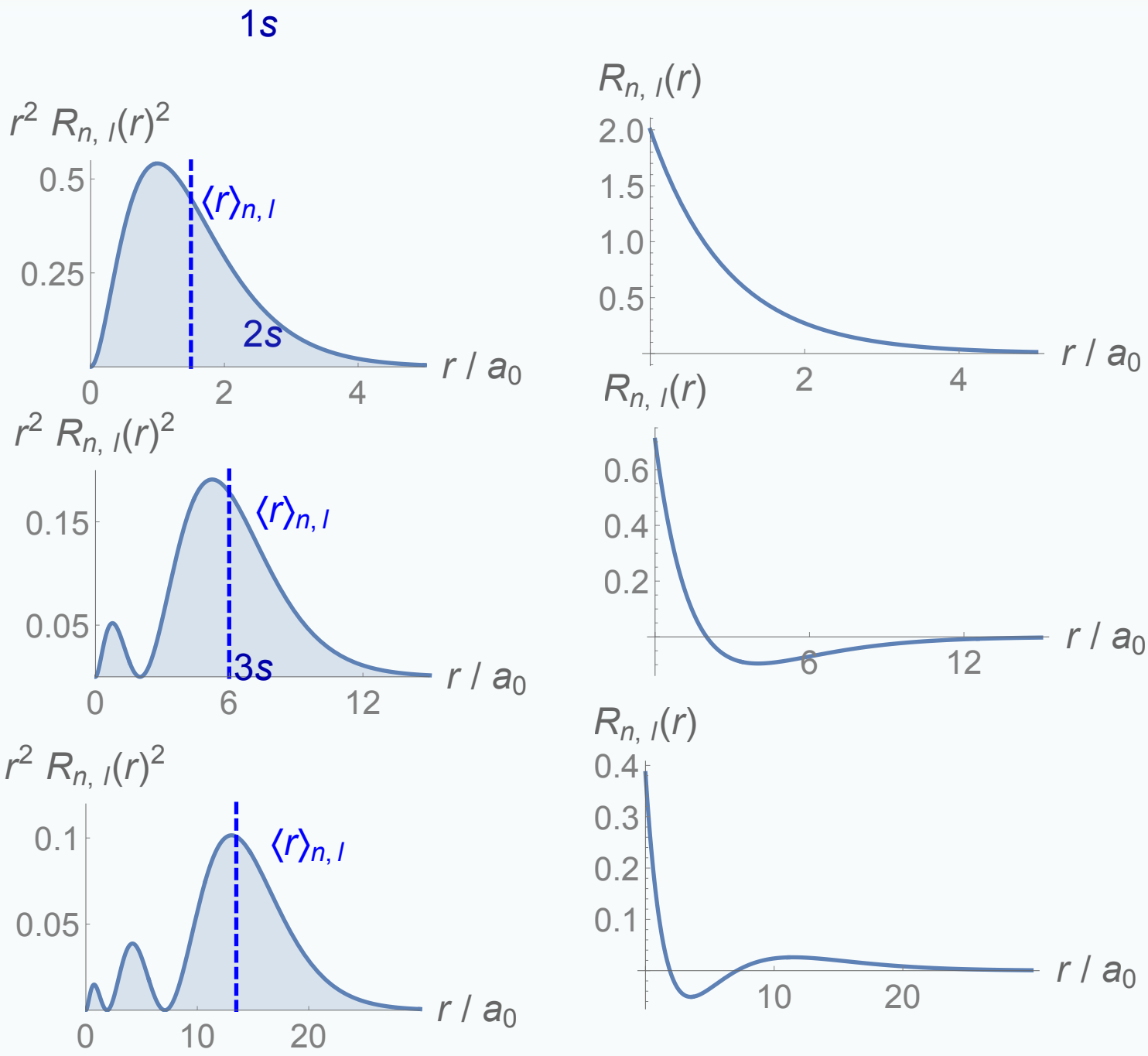

$r^2\ R_{n,\,l}(r)^2$
0.15
0.05
$\langle r \rangle_{n,\,l}$
0
6
12
$r\ /\ a_0$

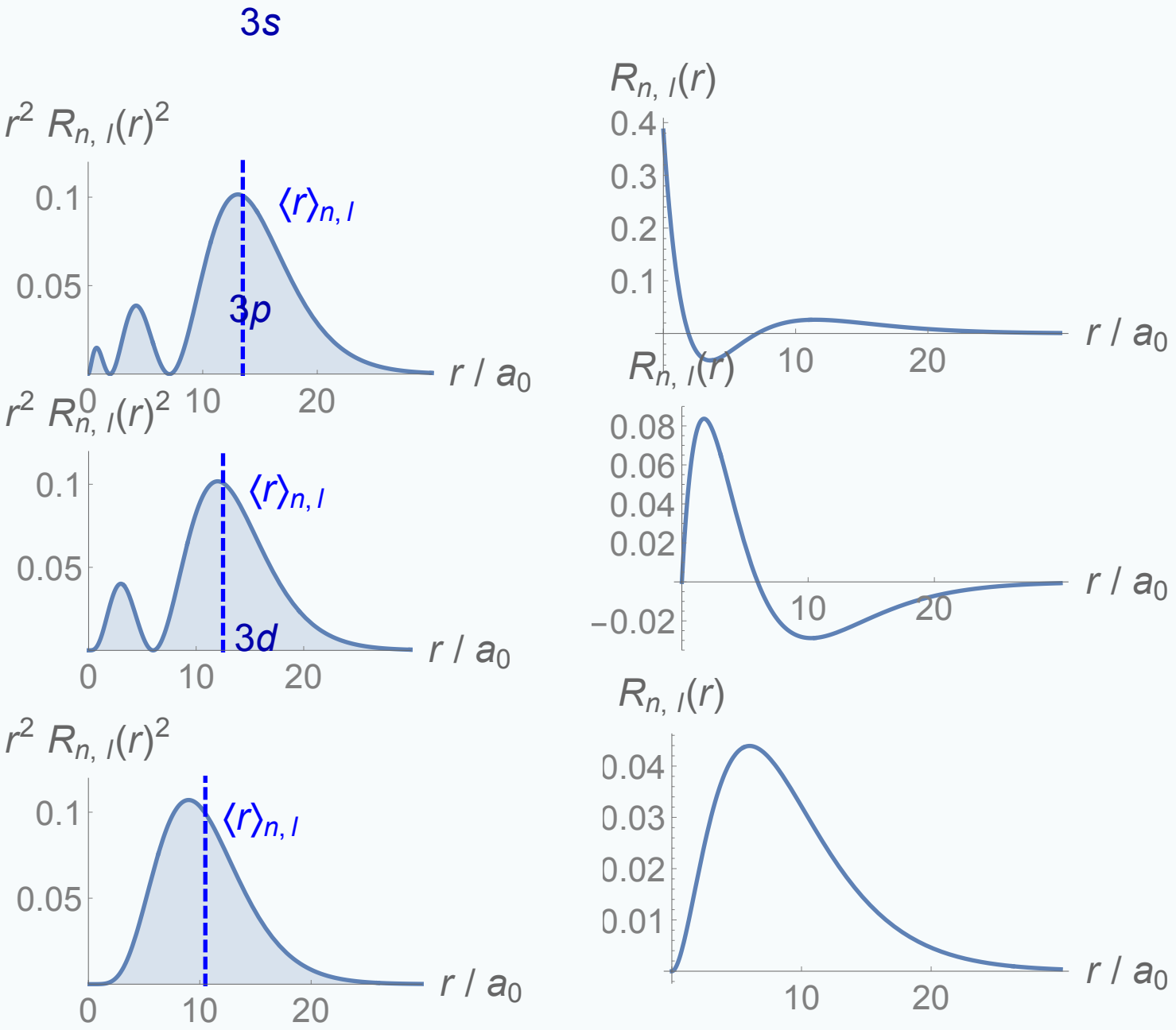

$R_{n,\,l}(r)$
0.6
0.4
0.2
6
12
$r\ /\ a_0$

2p

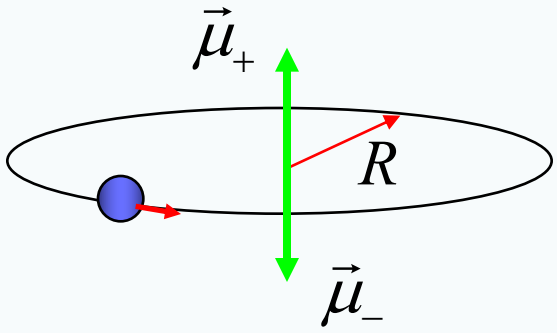

$r^2\ R_{n,\,l}(r)^2$
0.15
0.05
$\langle r \rangle_{n,\,l}$
0
6
12
$r\ /\ a_0$


$R_{n,\,l}(r)$
0.15
0.10
0.05
6
12
$r\ /\ a_0$


1s
$r^2\ R_{n,\,l}(r)^2$
0.5
0.25
$\langle r\rangle_{n,\,l}$
2s
0
2
4
$r\ /\ a_0$
$r^2\ R_{n,\,l}(r)^2$
0.15
0.05
$\langle r\rangle_{n,\,l}$
3s
0
6
12
$r\ /\ a_0$
$r^2\ R_{n,\,l}(r)^2$
0.1
0.05
$\langle r\rangle_{n,\,l}$
0
10
20
$r\ /\ a_0$
$R_{n,\,l}(r)$
2.0
1.5
1.0
0.5
2
4
$r\ /\ a_0$
$R_{n,\,l}(r)$
0.6
0.4
0.2
6
12
$r\ /\ a_0$
$R_{n,\,l}(r)$
0.4
0.3
0.2
0.1
10
20
$r\ /\ a_0$


3s
$r^2\ R_{n,\,l}(r)^2$
0.1
0.05
$\langle r\rangle_{n,\,l}$
3p
0
10
20
$r\ /\ a_0$
$r^2\ R_{n,\,l}(r)^2$
0.1
0.05
$\langle r\rangle_{n,\,l}$
3d
0
10
20
$r\ /\ a_0$
$r^2\ R_{n,\,l}(r)^2$
0.1
0.05
$\langle r\rangle_{n,\,l}$
0
10
20
$r\ /\ a_0$
$R_{n,\,l}(r)$
0.4
0.3
0.2
0.1
10
20
$r\ /\ a_0$
$R_{n,\,l}(r)$
0.08
0.06
0.04
0.02
−0.02
10
20
$r\ /\ a_0$
$R_{n,\,l}(r)$
0.04
0.03
0.02
0.01
10
20
$r\ /\ a_0$

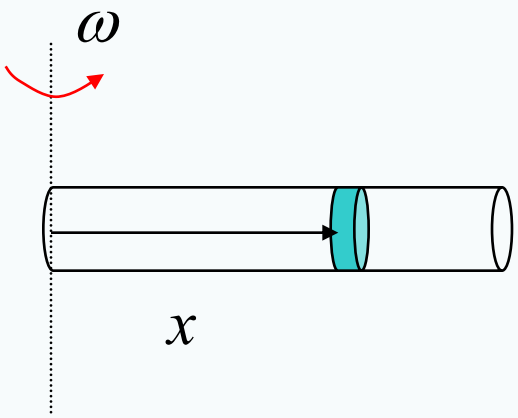
Magnetic moments



$$\vec{\mu} = I\vec{A} \qquad \vec{\mu} = \frac{q}{T}\pi R^2 \hat{\mathrm{n}} = \frac{1}{2} q\omega R^2 \hat{\mathrm{n}}$$

$$\vec{L} = \omega\vec{I} = m\omega R^2\,\hat{\mathrm{n}} \qquad \vec{\mu} = \frac{1}{2}\frac{q}{m}\vec{L}$$

$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

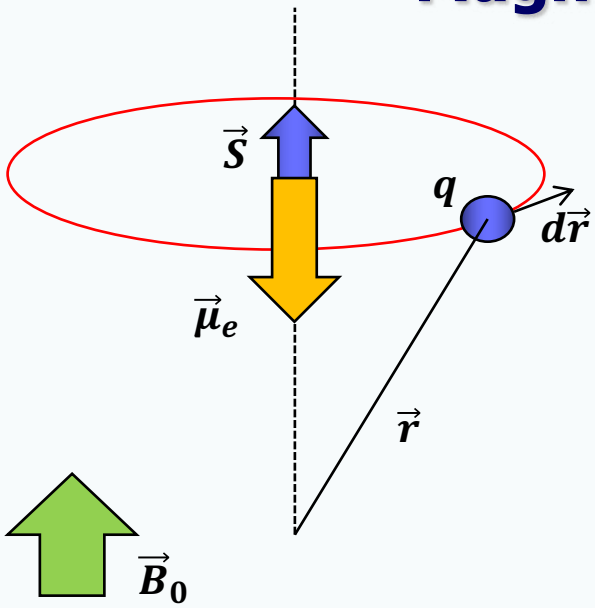


$$dI = \frac{\pi r^2 dx \rho\omega}{2\pi} \qquad A = \pi x^2$$

$$\mu = \frac{\pi r^2 \rho\omega}{2}\int_0^L x^2 dx = \frac{Q\omega L^2}{6}$$

$$I = \int_0^L x^2 dm = \rho\pi r^2 \int_0^L x^2 dx = \frac{1}{3}ML^2 \qquad \vec{\mu} = \frac{1}{2}\frac{Q}{M}\vec{L}$$

Magnetic properties of atoms



$$\vec{\mu} = I\vec{S} \qquad \vec{S} = \frac{1}{2}\oint(\vec{r}\times d\vec{r}) \qquad \vec{\mu} = \frac{1}{2m}\oint(\vec{r}\times\vec{p})dq$$

$$\vec{\mu_e} = -\frac{e}{2m}(\vec{r}\times\vec{p})$$

$$\hat{\mu} = -\frac{e}{2m}\hat{L} = \gamma\hat{L}$$

giromagnetic ratio for orbital electron

$$\mu_z = \gamma L_z = \gamma m\hbar = \mu_B m$$

the Bohr magneton

$$\mu_B = 9.274\ldots\times10^{-24}\text{J/T}$$

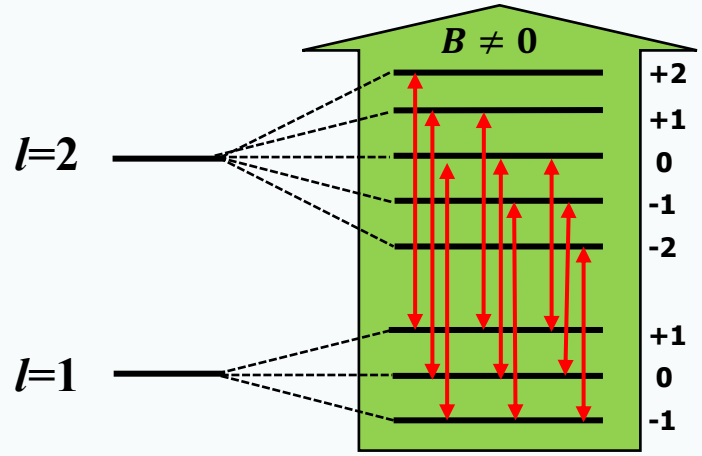
$$U_B = -\vec{\mu}\cdot\vec{B}_0 = \mu_B m B_{0z}$$

$$E_{n,l,m} = E_{Coulomb}(n) + \mu_B m B_{0z}$$

$$E = \hbar\omega$$

$$\frac{E}{L_z} = \frac{\hbar\omega}{\hbar} = \omega$$

for photons

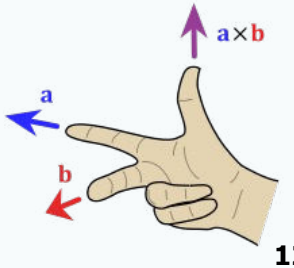


Photon emission: $\Delta l = \pm 1$

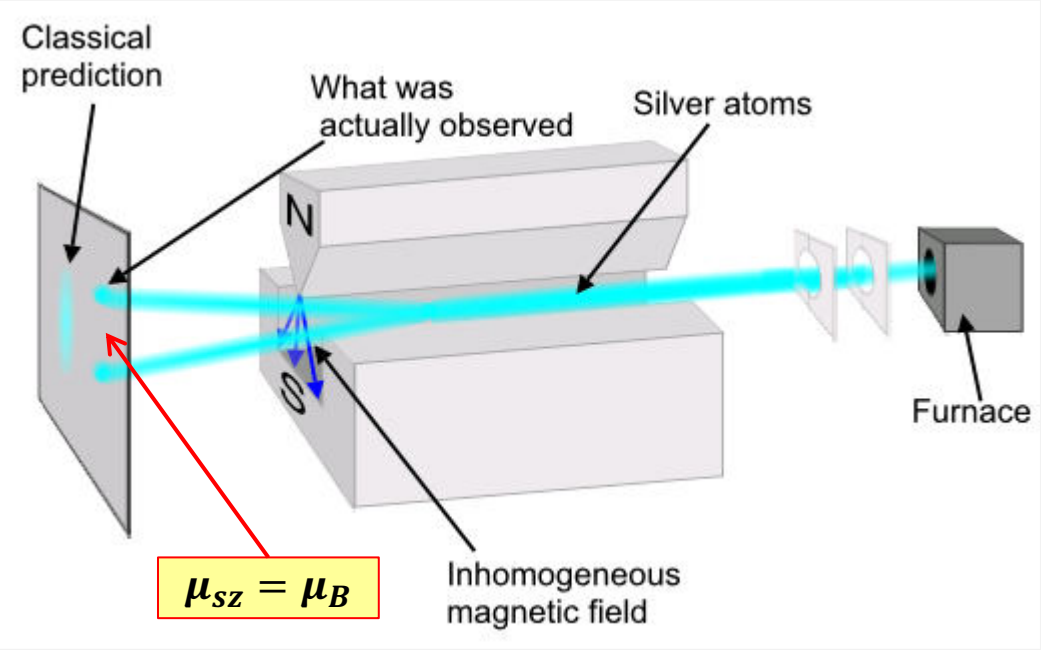
Photon spin: $s = 1$ (in $\hbar$ units)

$$L_s^2 = s(s+1)\hbar^2 = 2\hbar^2$$

$$\Delta m = \pm 1, 0$$



The Stern-Gerlach experiment



$$\vec{F} = \vec{\mu} \cdot \frac{\partial \vec{B}}{\partial \vec{r}}$$

$$l = 0 \Rightarrow m = 0$$

$$U_B = \mu_B m B_{0z} = 0 \ ?$$

Electron has intrinsic angular momentum l and related to it magnetic moment or spin S

$$\vec{\mu}_s = \gamma_s \vec{s}$$

$$-s \le m_s \le s \qquad 2s + 1 = 2 \Rightarrow s = 1/2$$

$$|\vec{s}| = \sqrt{s(s+1)}\hbar$$

$$\mu_z = \gamma L_z = \gamma m \hbar = \mu_B m$$ - orbiting electron

$$\frac{\mu_{sz}}{s_z} = \gamma_s = \frac{\mu_B}{\frac{1}{2}\hbar} = 2\frac{\mu_B}{\hbar} = 2\gamma$$

For a free-standing electron:

$$|\vec{\mu}_s| = g_e \mu_B \sqrt{s(s+1)}$$

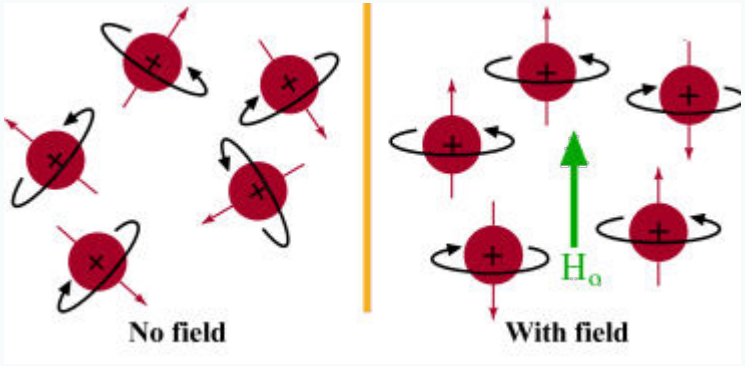
-2.00231930436153

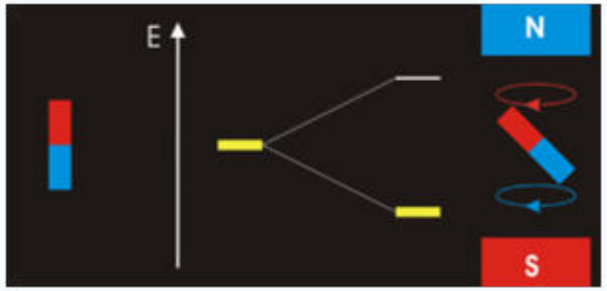
For a free-standing proton:

5.585694713

$$|\vec{\mu}_p| = g_p \mu_N \sqrt{s(s+1)}$$

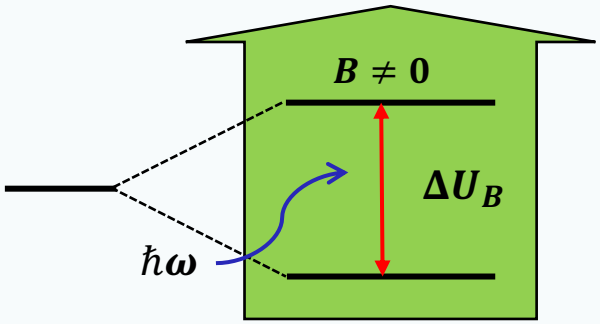
Electron paramagnetic resonance





$$U_B = -\vec{\mu} \cdot \vec{B}_0 \qquad |\vec{\mu}_s| = g_e \mu_B \sqrt{s(s+1)}$$

$$U_B = g_e \mu_B m_s B_{0z} = \pm \frac{1}{2} g_e \mu_B B_{0z}$$



$$\Delta U_B = g_e \frac{e\hbar}{2m_e} B_{0z} \qquad E = \hbar\omega = g_e \frac{e\hbar}{2m_e} B_{0z}$$

$$\omega = g_e \frac{e}{2m_e} B_{0z} \approx 1.76 \times 10^{11} \left[\text{rad s}^{-1}\text{T}^{-1}\right] \times B_{0z}$$

$$\nu(280\ mT) \approx 7,8\ GHz \qquad \nu(1\ mT) \approx 28\ MHz$$

Stationary states

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + U(\mathbf{r})\Psi$$

If Ψ in the whole space is known at certain instant of time, then Ψ can be determined at any other instances.

If Ψ_1 and Ψ_2 are two solutions of the Schrödinger equation, then $a_1\Psi_1 + a_2\Psi_2$ is also solution (superposition).

Stationary states:

$$\psi = \psi(\mathbf{r})e^{-i\omega t}$$

function of time only

function of space only

$$\rho = \psi\psi^* = \psi(\mathbf{r})\psi^*(\mathbf{r})$$

$$E\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\psi$$

Schrödinger's equation for stationary states

$$E_{total}\psi = \left[E_{kin} + U(\mathbf{r})\right]\psi$$

Energy conservation in quantum mechanics

Superposition principle applies too! But superposition of two stationary state solutions will not be stationary state!

$$\Psi_1 = \psi_1(\mathbf{r})e^{-i\omega_1 t}$$

$$\Psi_2 = \psi_2(\mathbf{r})e^{-i\omega_2 t}$$

$$\psi_1(\mathbf{r}) = A_1 e^{-i\delta_1}$$

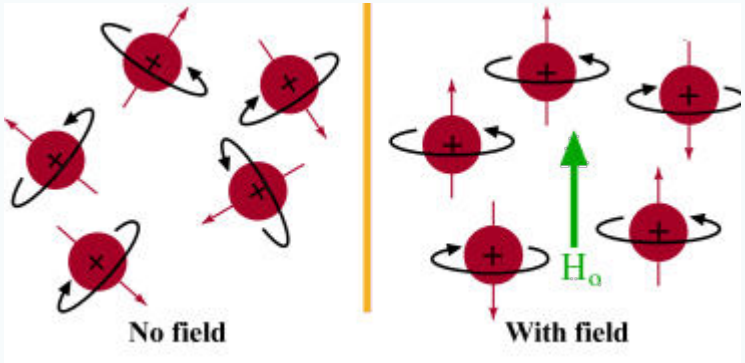
$$\psi_2(\mathbf{r}) = A_2 e^{-i\delta_2}$$

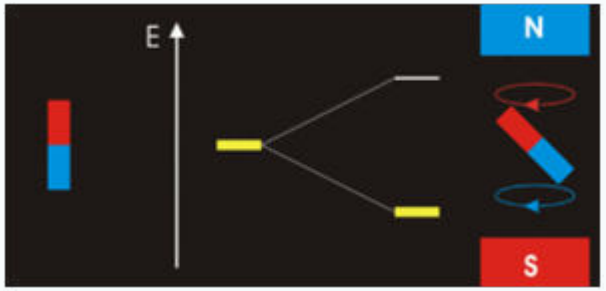
$$\left|\Psi_1 + \Psi_2\right|^2 = \left(\psi_1(\mathbf{r})e^{-i\omega_1 t} + \psi_2(\mathbf{r})e^{-i\omega_2 t}\right)\left(\psi_1^*(\mathbf{r})e^{i\omega_1 t} + \psi_2^*(\mathbf{r})e^{i\omega_2 t}\right)$$

$$= \left|\psi_1(\mathbf{r})\right|^2 + \left|\psi_2(\mathbf{r})\right|^2 + \psi_1(\mathbf{r})\psi_2^*(\mathbf{r})e^{-i(\omega_1-\omega_2)t} + \psi_2(\mathbf{r})\psi_1^*(\mathbf{r})e^{-i(\omega_2-\omega_1)t}$$

$$= \left|A_1\right|^2 + \left|A_2\right|^2 + 2\left|A_1\right|\left|A_2\right|\cos\left((\omega_2-\omega_1)t + (\delta_2-\delta_1)\right)$$

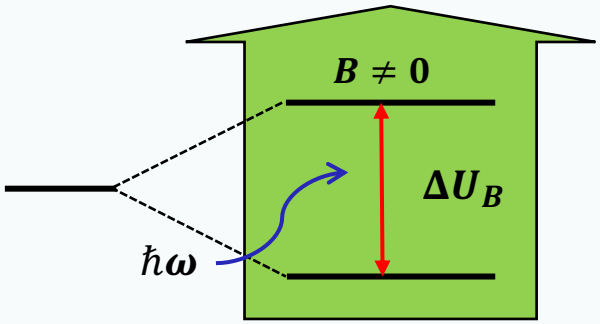
Nuclear magnetic resonance





$$U_B = -\vec{\mu} \cdot \vec{B}_0 \qquad |\vec{\mu}_p| = g_p \mu_N \sqrt{s(s+1)}$$

$$U_B = g_p \mu_N m_s B_{0z} = \pm \frac{1}{2} g_p \frac{e\hbar}{2m_p} B_{0z}$$



$$\Delta U_B = g_p \frac{e\hbar}{2m_p} B_{0z} \qquad E = \hbar\omega = g_p \frac{e\hbar}{2m_p} B_{0z}$$

$$\omega = g_p \frac{e}{2m_p} B_{0z} \approx 2.67 \times 10^8 \left[\text{rad s}^{-1}\text{T}^{-1}\right] \times B_{0z}$$

$$\nu(280\ mT) \approx 19\ MHz$$

Electron paramagnetic resonance

$$\omega = \frac{2e}{2m_e} B_{0z} \approx 1.76 \times 10^{11}\ B_{0z}$$

NMR Nobel prize laureates

Physics

1943

Otto Stern
CIT, USA

1944

Isidor Rabi
Columbia Uni., USA

1952

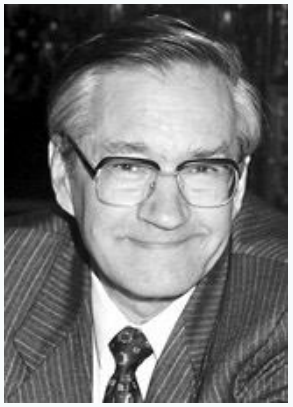
Felix Bloch
Stanford, USA

1952

Edward Purcell
Harvard, USA

Chemistry

1991



Richard R. Ernst
ETH, Switzerland

2002

Kurt Wüthrich
ETH, Switzerland

Medicine

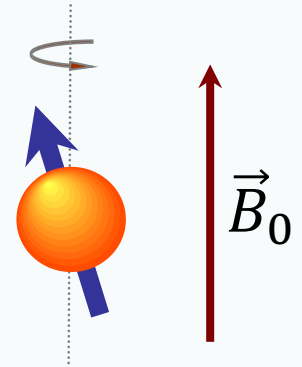
2003

Paul Lauterbur
Urbana, USA

2003

Peter Mansfield
Nottingham, UK

Ethanol



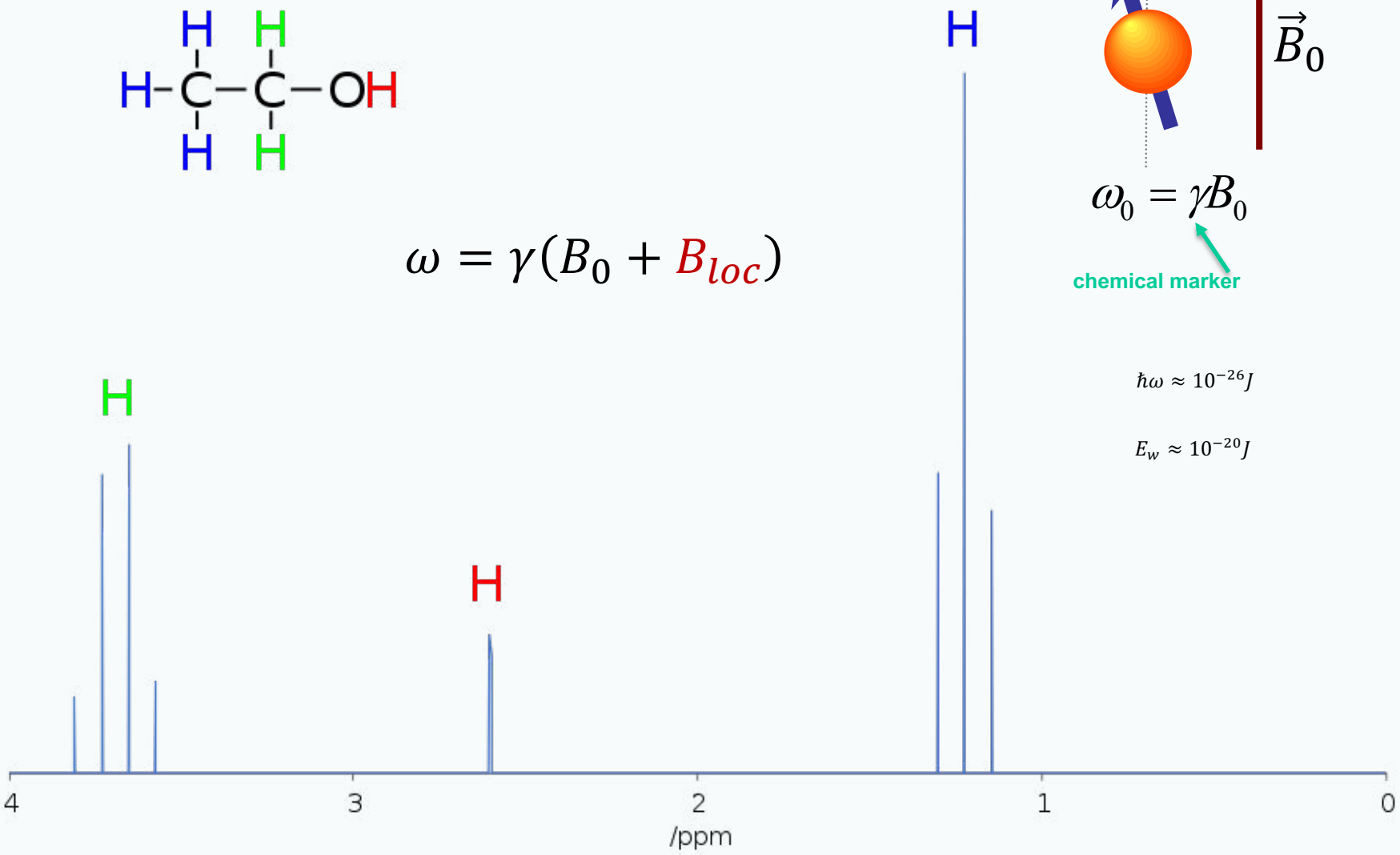
$$\omega_0 = \gamma B_0$$

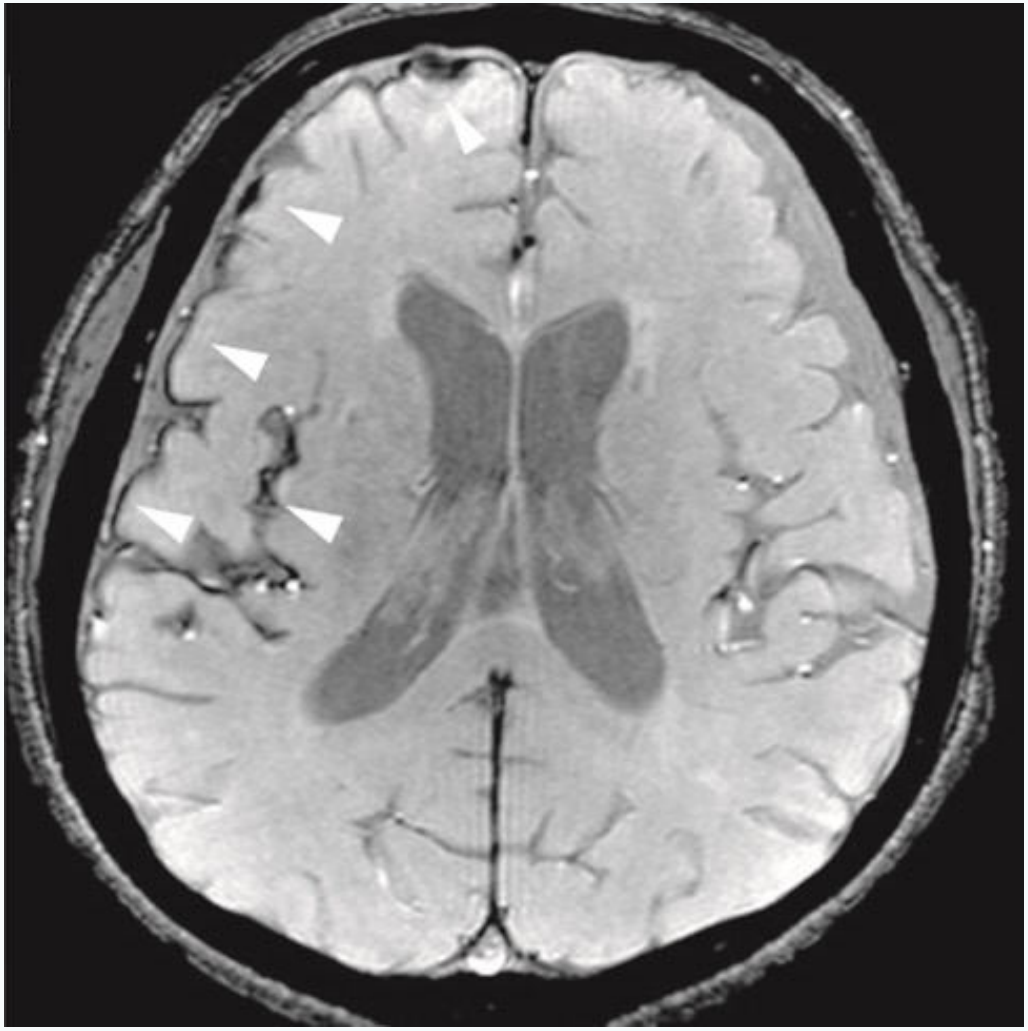
chemical marker

$$\omega = \gamma(B_0 + B_{loc})$$

$\hbar\omega \approx 10^{-26} J$

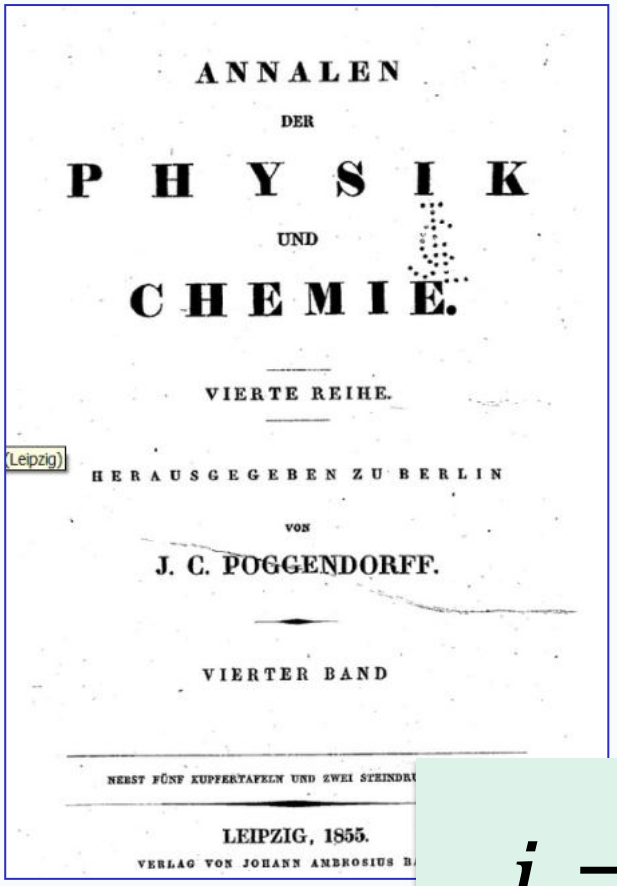
$E_w \approx 10^{-20} J$





$$\omega = \gamma(B_0[x, y, z] + B_{loc})$$

In 1855 Adolf Fick publishes his seminal work on diffusion in Annalen der Physik und Chemie printed in Leipzig



ANNALEN

DER

PHYSIK

UND

CHEMIE.

VIERTE REIHE.

(Leipzig)

HERAUSGEGEBEN ZU BERLIN

VON

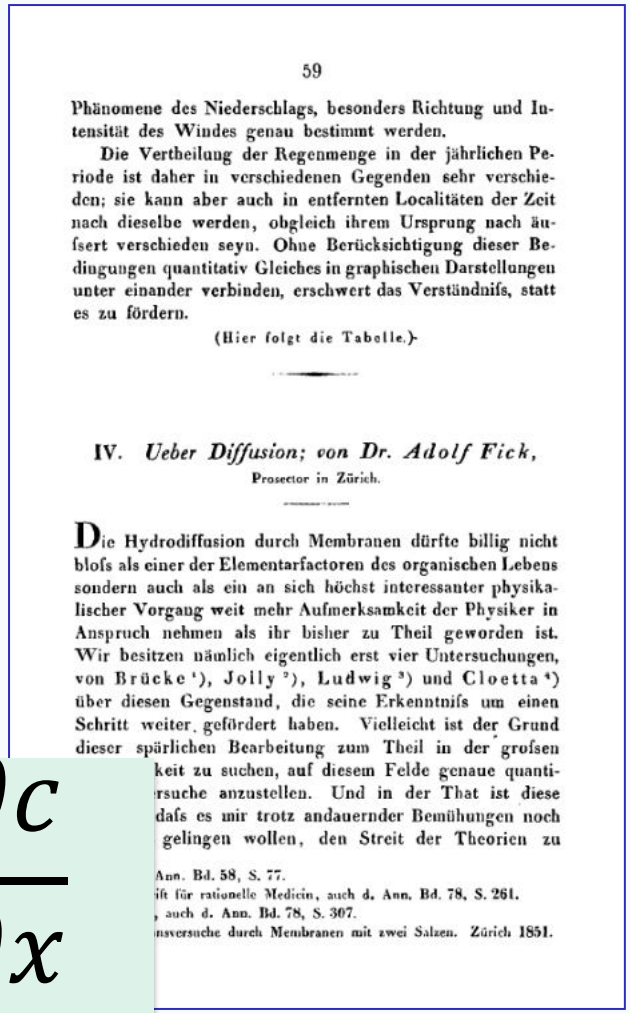
J. C. POGGENDORFF.

VIERTER BAND

NEBST FÜNF KUPFERTAFELN UND ZWEI STEINDR

LEIPZIG, 1855.

VERLAG VON JOHANN AMBROSIUS B



59

Phänomene des Niederschlags, besonders Richtung und Intensität des Windes genau bestimmt werden.

Die Vertheilung der Regenmenge in der jährlichen Periode ist daher in verschiedenen Gegenden sehr verschieden; sie kann aber auch in entfernten Localitäten der Zeit nach dieselbe werden, obgleich ihrem Ursprung nach äufsert verschieden seyn. Ohne Berücksichtigung dieser Bedingungen quantitativ Gleiches in graphischen Darstellungen unter einander verbinden, erschwert das Verständnifs, statt es zu fördern.

(Hier folgt die Tabelle.)

IV. *Ueber Diffusion; von Dr. Adolf Fick,*

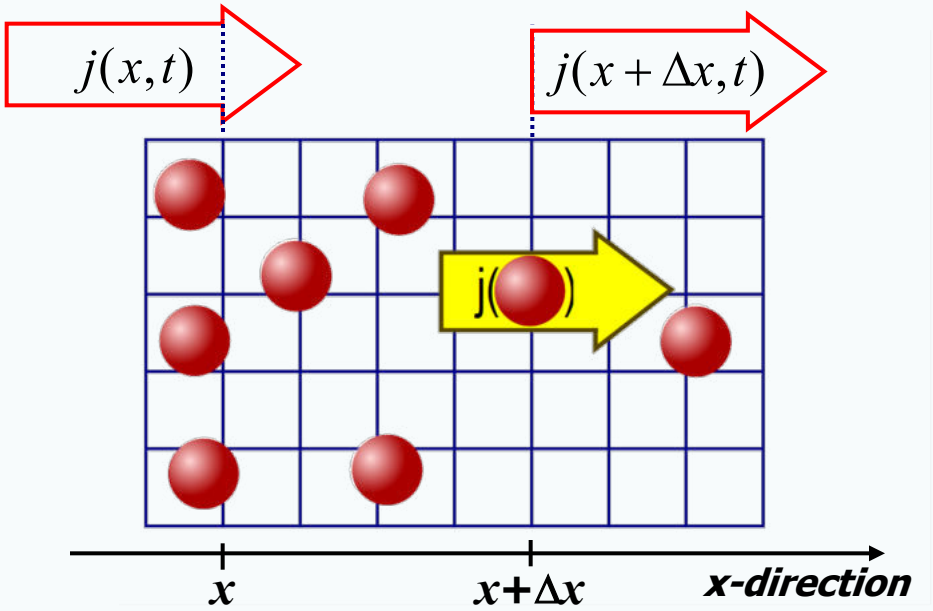
Prosector in Zürich.

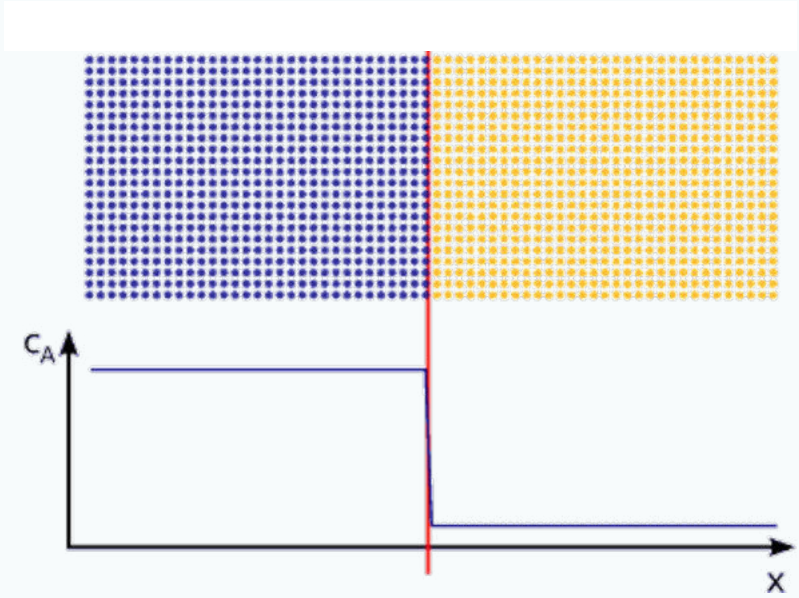
Die Hydrodiffusion durch Membranen dürfte billig nicht blofs als einer der Elementarfactoren des organischen Lebens sondern auch als ein an sich höchst interessanter physikalischer Vorgang weit mehr Aufmerksamkeit der Physiker in Anspruch nehmen als ihr bisher zu Theil geworden ist. Wir besitzen nämlich eigentlich erst vier Untersuchungen, von Brücke [1]), Jolly [2]), Ludwig [3]) und Cloetta [4]) über diesen Gegenstand, die seine Erkenntnifs um einen Schritt weiter gefördert haben. Vielleicht ist der Grund dieser spärlichen Bearbeitung zum Theil in der grofsen keit zu suchen, auf diesem Felde genaue quanti- rsuche anzustellen. Und in der That ist diese dafs es mir trotz andauernder Bemühungen noch gelingen wollen, den Streit der Theorien zu

Ann. Bd. 58, S. 77.
ift für rationelle Medicin, auch d. Ann. Bd. 78, S. 261.
, auch d. Ann. Bd. 78, S. 307.
nsversuche durch Membranen mit zwei Salzen. Zürich 1851.

$$j = -D \frac{\partial c}{\partial x}$$

Diffusion flux under concentration gradient



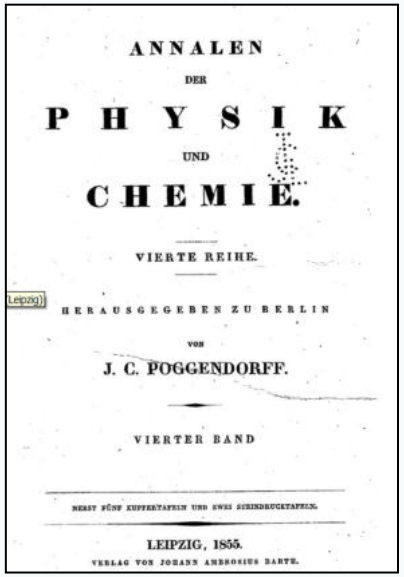


1st Fick's law + **Mass conservation**

$$j = -D\frac{\partial c}{\partial x} \qquad \frac{\partial c}{\partial t} = \frac{j_x(x) - j_x(x+\Delta x)}{\Delta x} \approx -\frac{\partial j}{\partial x}$$

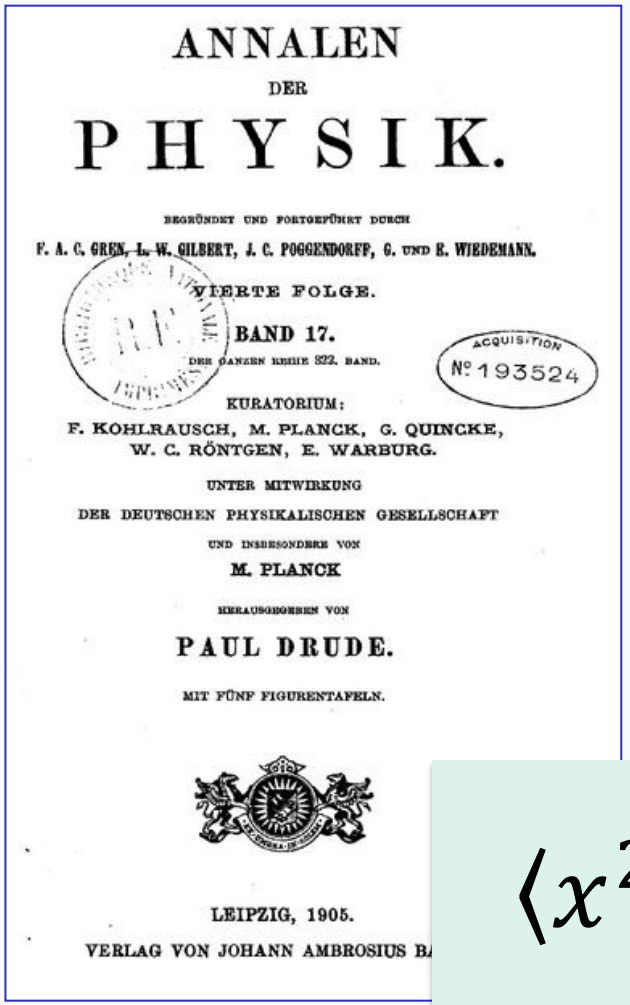
2nd Fick's law
Diffusion equation

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2}$$


ANNALEN
DER
PHYSIK
UND
CHEMIE.
VIERTE REIHE.
HERAUSGEGEBEN ZU BERLIN
VON
J. C. POGGENDORFF.
VIERTER BAND
LEIPZIG, 1855.

A. Fick, Über Diffusion. Ann. Phys. Chem., 1855, 94, 59

In 1905 Albert Einstein publishes his famous work on diffusion in Annalen der Physik printed in Leipzig



ANNALEN
DER
PHYSIK.

BEGRÜNDET UND FORTGEFÜHRT DURCH
F. A. C. GREN, L. W. GILBERT, J. C. POGGENDORFF, G. UND E. WIEDEMANN.

VIERTE FOLGE.

BAND 17.

DER GANZEN REIHE 322. BAND.

ACQUISITION
Nº 193524

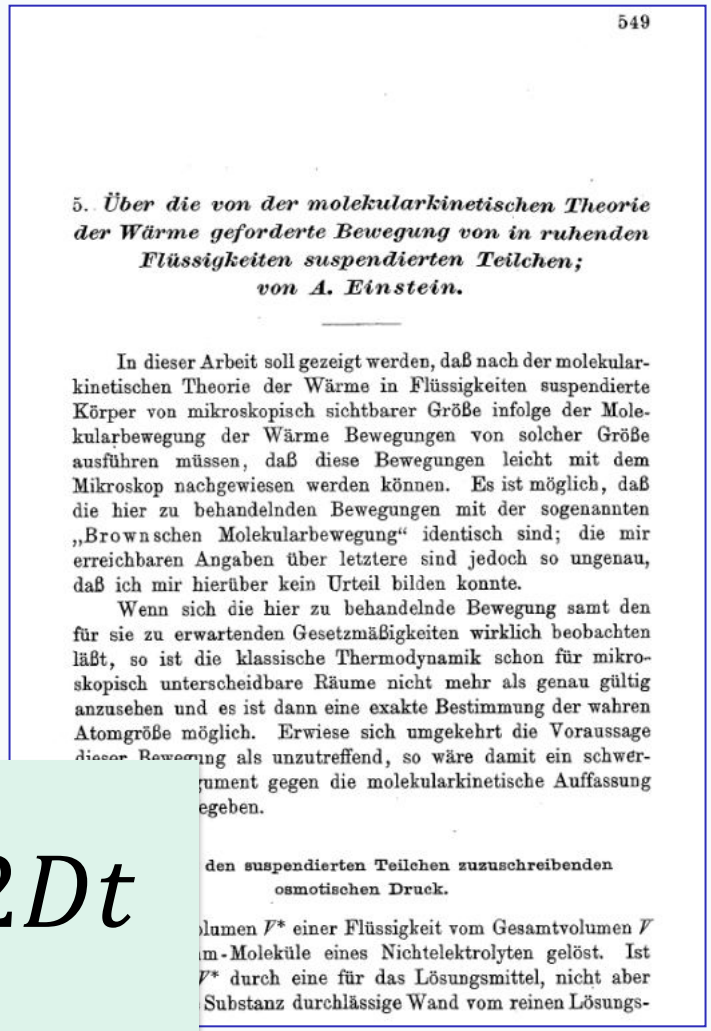
KURATORIUM:
F. KOHLRAUSCH, M. PLANCK, G. QUINCKE,
W. C. RÖNTGEN, E. WARBURG.

UNTER MITWIRKUNG
DER DEUTSCHEN PHYSIKALISCHEN GESELLSCHAFT
UND INSBESONDERE VON
M. PLANCK

HERAUSGEGEBEN VON
PAUL DRUDE.

MIT FÜNF FIGURENTAFELN.

LEIPZIG, 1905.
VERLAG VON JOHANN AMBROSIUS BA



549

5. *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen;*
von A. Einstein.

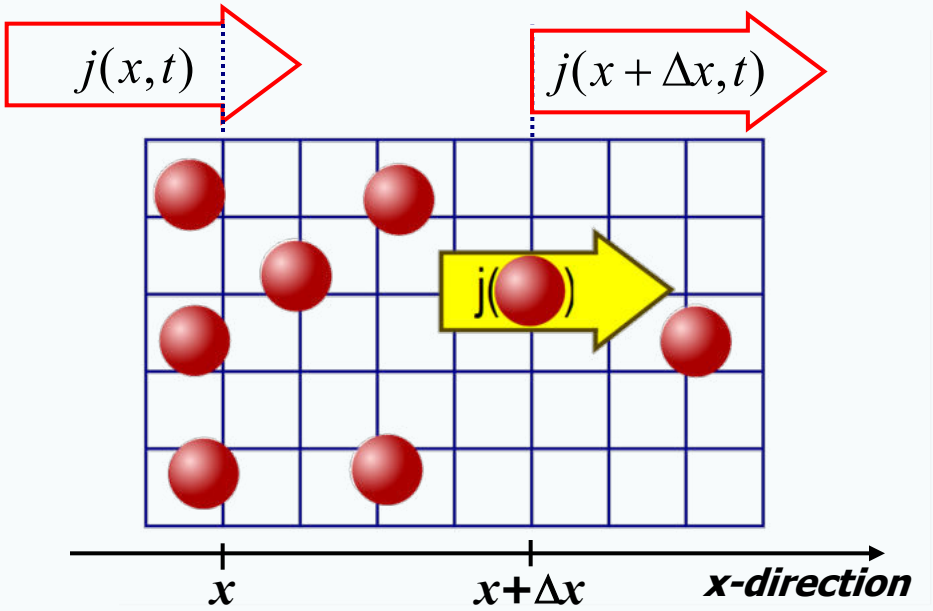
In dieser Arbeit soll gezeigt werden, daß nach der molekularkinetischen Theorie der Wärme in Flüssigkeiten suspendierte Körper von mikroskopisch sichtbarer Größe infolge der Molekularbewegung der Wärme Bewegungen von solcher Größe ausführen müssen, daß diese Bewegungen leicht mit dem Mikroskop nachgewiesen werden können. Es ist möglich, daß die hier zu behandelnden Bewegungen mit der sogenannten „Brownschen Molekularbewegung" identisch sind; die mir erreichbaren Angaben über letztere sind jedoch so ungenau, daß ich mir hierüber kein Urteil bilden konnte.

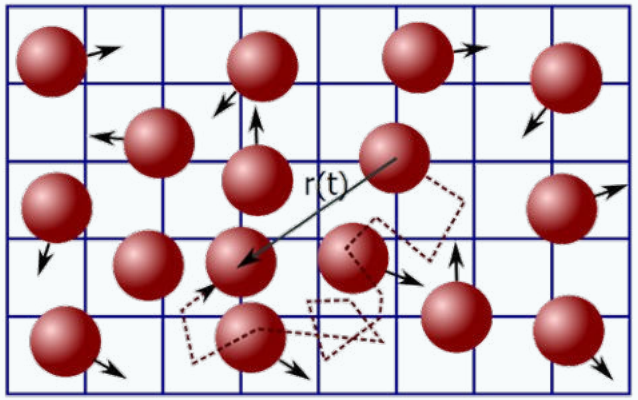
Wenn sich die hier zu behandelnde Bewegung samt den für sie zu erwartenden Gesetzmäßigkeiten wirklich beobachten läßt, so ist die klassische Thermodynamik schon für mikroskopisch unterscheidbare Räume nicht mehr als genau gültig anzusehen und es ist dann eine exakte Bestimmung der wahren Atomgröße möglich. Erwiese sich umgekehrt die Voraussage dieser Bewegung als unzutreffend, so wäre damit ein schwerument gegen die molekularkinetische Auffassung egeben.

den suspendierten Teilchen zuzuschreibenden osmotischen Druck.

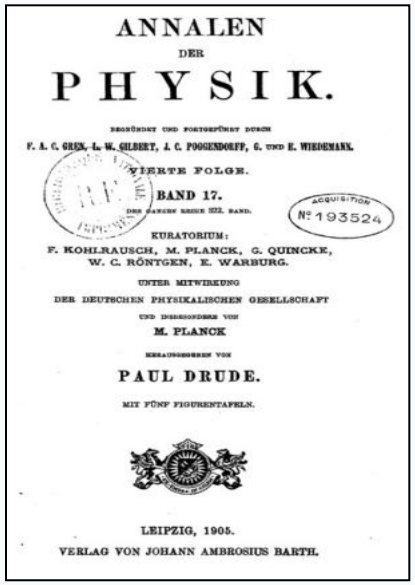
lumen V^* einer Flüssigkeit vom Gesamtvolumen V m-Moleküle eines Nichtelektrolyten gelöst. Ist V^* durch eine für das Lösungsmittel, nicht aber Substanz durchlässige Wand vom reinen Lösungs-

$$\langle x^2 \rangle = 2Dt$$





$$\langle x^2(t)\rangle = 2Dt$$



2nd Fick's law
Diffusion equation

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2}$$

A. Einstein, Ann. Phys., 1905, 17, 54

In 1946 Felix Bloch publishes the Bloch equations and demonstrate with colleagues the first NMR signal

PHYSICAL REVIEW VOLUME 70, NUMBERS 7 AND 8 OCTOBER 1 AND 15, 1946

Nuclear Induction

F. BLOCH
Stanford University, California
(Received July 19, 1946)

The magnetic moments of nuclei in normal matter will result in a nuclear paramagnetic polarization upon establishment of equilibrium in a constant magnetic field. It is shown that a radiofrequency field at right angles to the constant field causes a forced precession of the total polarization around the constant field with decreasing latitude as the Larmor frequency approaches adiabatically the frequency of the r-f field. Thus there results a component of the nuclear polarization at right angles to both the constant and the r-f field and it is shown that under normal laboratory conditions this component can induce observable voltages. In Section 3 we discuss this nuclear induction, considering the effect of external fields only, while in Section 4 those modifications are described which originate from internal fields and finite relaxation times.

1. INTRODUCTION

THE method of magnetic resonance[1] has been successfully applied to measure the magnetic moment of the neutron[2] and of various nuclei.[3] The principal feature of this method is the observation of transitions, caused by resonance of an applied radiofrequency field with the Larmor precession of the moments around a constant magnetic field. In its application to nuclear moments the deflection of molecular beams in an inhomogeneous field was used as a means of detecting the occurrence of nuclear transitions. This method of detection has proven to be very fruitful but it was clear, at the same time, that the connection between molecular beams and magnetic resonance was not of basic character. The question arose, in particular, whether nuclear transitions could not be detected by far simpler electromagnetic methods, applied to matter of ordinary density.[4]

An attempt in this direction was undertaken by Gorter and Broer[5] whose arrangement was designed to indicate magnetic resonance absorption by a sl... electric oscillator... upon consideratio... radiofrequency fi...

they cause only a slight disturbance of the spin orientation; it was carried out with LiCl and KF at low temperatures and it was suggested that the failure to find an effect was caused by the fact that the nuclei had not found the orientation, corresponding to thermal equilibrium.

The first successful experiments to detect magnetic resonance by electromagnetic effects have been carried out recently and independently in the physics laboratories of Harvard[6] and Stanford[7] Universities. The experiment of Purcell and his collaborators is very closely connected to that of Gorter and Broer, the main difference being that resonance absorption manifests itself in the change of Q of an electric oscillator rather than in a change of frequency, and it presupposes, likewise, the necessity of only slightly perturbing r-f fields.

The considerations upon which our work was based have several features in common with the two experiments, previously mentioned, but differ rather essentially in others. In the first place, the radiofrequency field is deliberately

[1] I. I. Rabi, Phys. R...
[2] L. W. Alvarez a... (1940).
[3] I. I. Rabi, S. Milb... Phys. Rev. **53**, 318 (1...
[4] The first purely m... due to nuclear mome... of liquid hydrogen wi... L. W. Schubnikow, Sc...
[5] C. J. Gorter and L...

$$\dot{M}_x-\gamma(M_yH_z-M_zH_y)+\frac{1}{T_2}M_x=0, \qquad (38a)$$

$$\dot{M}_y-\gamma(M_zH_x-M_xH_z)+\frac{1}{T_2}M_y=0, \qquad (38b)$$

$$\dot{M}_z-\gamma(M_xH_y-M_yH_x)+\frac{1}{T_1}M_z=\frac{1}{T_1}M_0. \qquad (38c)$$

(5) As in comparing the moments of neutron, proton, and deuteron, nuclear induction can well be developed as a simple and practical method to calibrate and measure high magnetic fields with great accuracy, and to apply it, for example, in the construction of cyclotrons and mass spectrographs.

There are unquestionably more problems which will become tangible in further development of the new electromagnetic effects. The fact that they are simple to obtain and require only very modest equipment should make it possible for many investigators to enter this field of research.

PHYSICAL REVIEW VOLUME 70, NUMBERS 7 AND 8 OCTOBER 1 AND 15, 1946

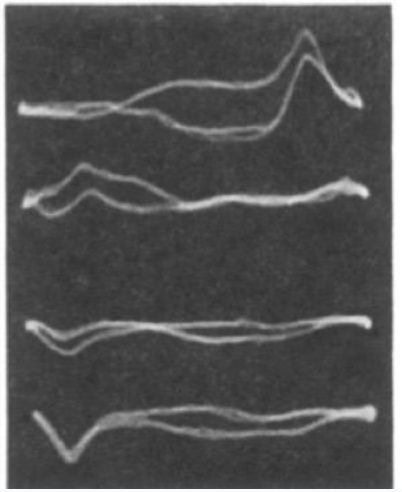
The Nuclear Induction Experiment

F. BLOCH, W. W. HANSEN, AND M. PACKARD
Stanford University, California
(Received July 19, 1946)

The phenomenon of nuclear induction has been studied experimentally. The apparatus used is described, both as to principle and detail. Experiments have been carried out in which the signals from protons contained in a variety of substances were observed. The results show the role played by the relaxation time, which was found to vary between about 10^{-4} second and many seconds.

INTRODUCTION

IN this paper we aim to describe certain experiments designed to study the phenomenon of nuclear induction, the theory of which is described in the preceding paper. While it will be



we can expect the polarization vector to deviate appreciably from the z direction if the z field H_0 approaches the resonance value H^* given by

$$|\gamma|H^*=\omega, \qquad (3)$$

where γ, the gyromagnetic ratio, is the ratio of nuclear moment to angular momentum characteristic of the nuclei under consideration. Quantitatively, the result of this deviation may be described by a macroscopic polarization vector **M** with components given by Eq. (44) of I,

$$M_x=\frac{M}{(1+\delta^2)^{\frac{1}{2}}}\cos\omega t, \qquad (4a)$$

$$M_y=\mp\frac{M}{(1+\delta^2)^{\frac{1}{2}}}\sin\omega t, \qquad (4b)$$

$$M_z=\frac{M}{(1+\delta^2)^{\frac{1}{2}}}, \qquad (4c)$$

where

$$\delta=(H_0-H^*)/H_1$$

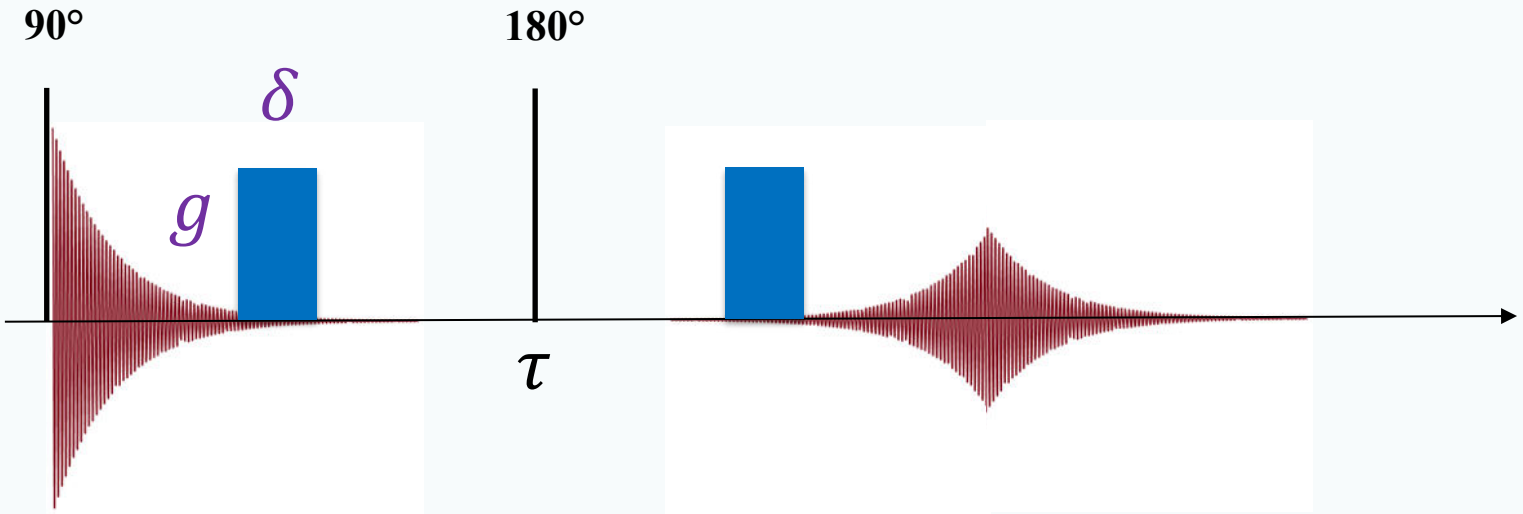
is the deviation of z field H_0 from its resonance value H^* in units of the half-amplitude H_1 of the oscillating x field. The ambiguous sign in (4b) is to allow for the possibility of either positive or negative values of γ. The quantity M depends in

Pulsed Field Gradient NMR is the most direct experimental approach to probe the mean-square-displacements

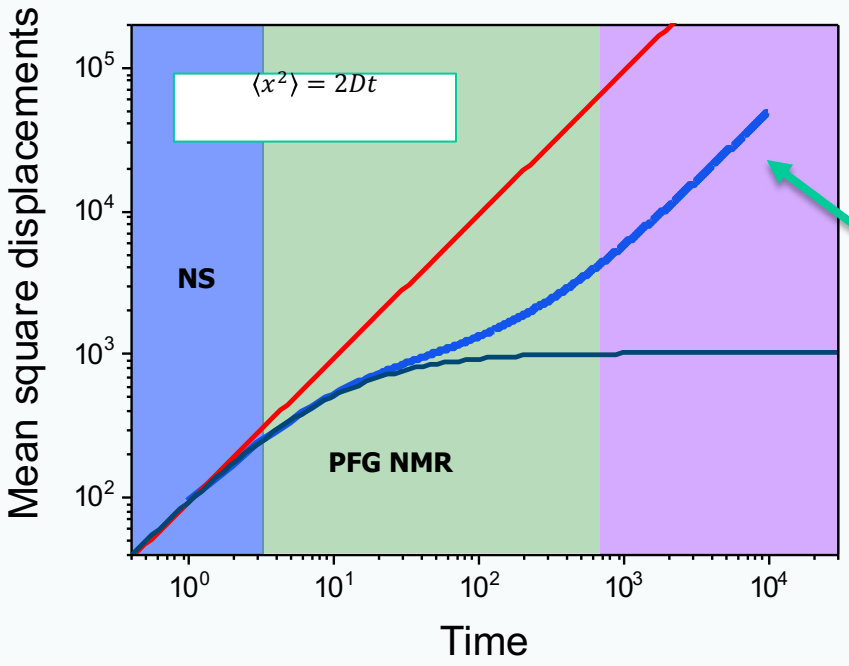
$$\langle \varphi^2(2\tau) \rangle = \gamma^2 g^2 \int_0^{\delta} \int_{\tau}^{\tau+\delta} \langle z(t') z(t'') \rangle dt' dt'' = \gamma^2 g^2 \delta^2 \langle \Delta z^2(\tau) \rangle$$

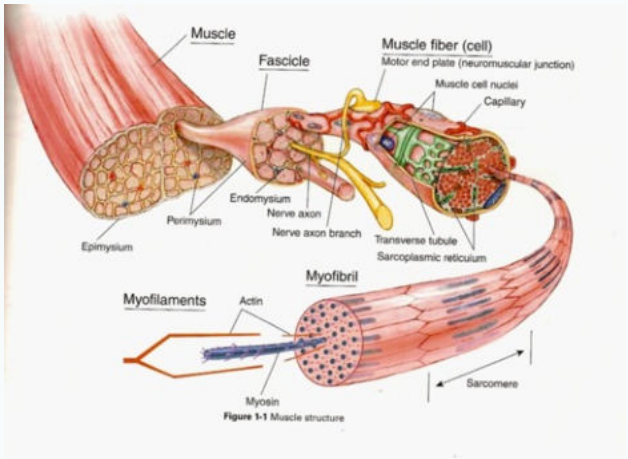
$$S(2\tau) = e^{-\frac{1}{2}\langle \varphi^2(2\tau) \rangle} = e^{-\frac{1}{2} q^2 \langle \Delta z^2(\tau) \rangle}$$

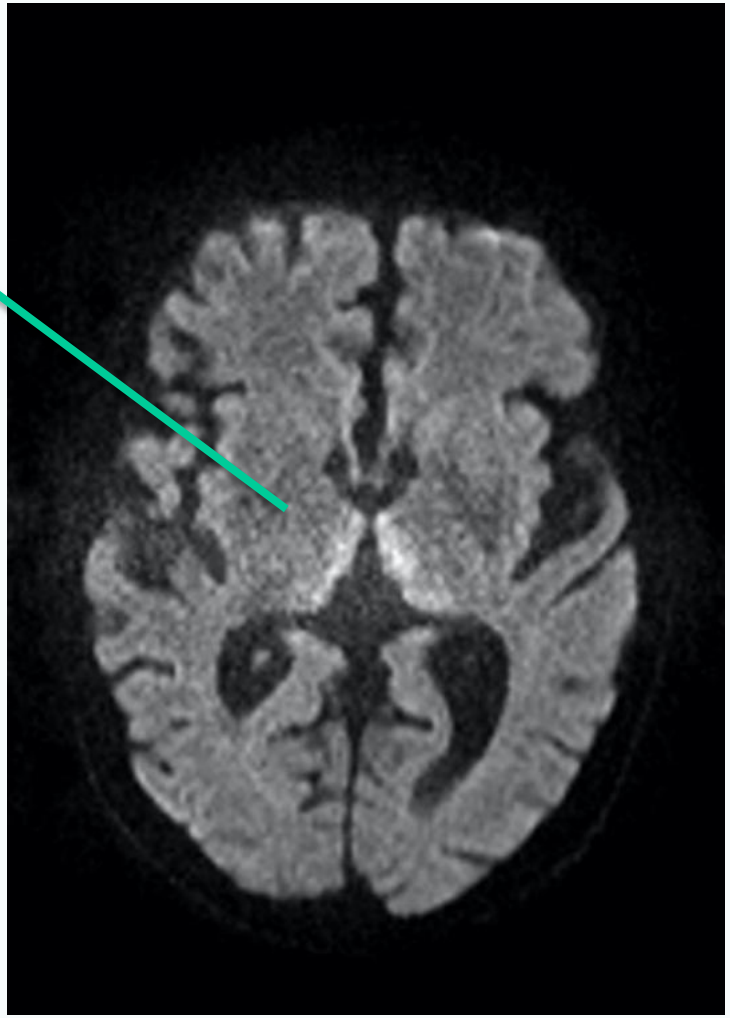
$$q = \gamma \delta g$$



Failing biophysical models for MRI contrasts







Diffusion-weghted MRI

Applied Magnetic Resonance
Felix Bloch Institute for Solid State Physics
University of Leipzig

To remember!

- **Quantum mechanical calculations reproduce the atomic energy levels as obtained using the Bohr's model.**
- **The calculations predict however n^2-fold degeneracy of the levels.**
- **For s-orbitals the radial electron density distribution function is spherically symmetric, for others - not.**
- **The orbital angular momentum gives rise to magnetic properties of atoms.**
- **The electrons and protons have intrinsic angular momentum. Hence magnetic moment as well.**
- **There are selection rules for spontaneous emmision of photons: $\Delta l = \pm 1$; $\Delta m = 0, \pm 1$.**