NEW VISION OF SPIN NUTATION

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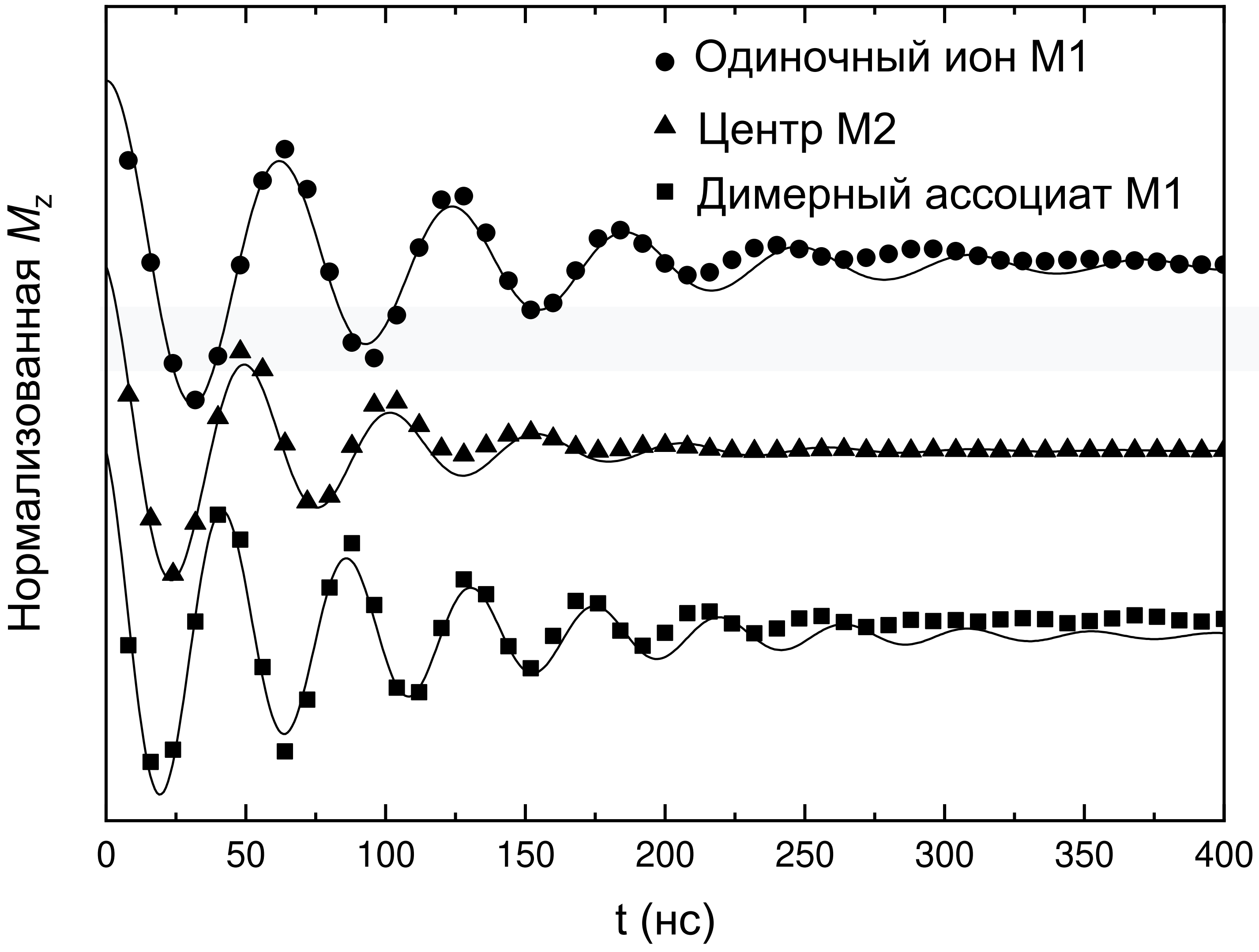
What is nutation?

When you suddenly turn on a microwave field, the motion of the magnetization in the transient time scale is called nutation



This work was initiated by experiments by A.A. Sukhanov, V.F. Tarasov

Yb^{3+} в Mg_2SiO_4

Current situation

While nutation is used in NMR spectroscopy,
it is less used in EPR spectroscopy.

This is because the theory of the transient nutation method is much less developed than the theory of steady-state EPR spectra.

Therefore, it is difficult to extract the magnetic resonance parameters of the spin system from EPR experimental data.

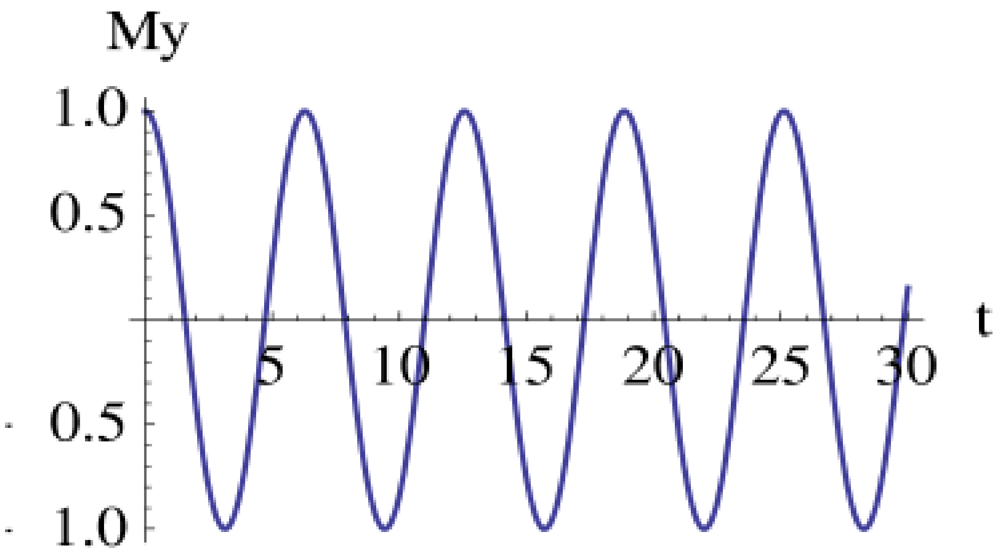
There are reasons to believe that the nutation method may be good for measuring the magnitude of the electron spins.

The value of the total spin of unpaired electrons is an important characteristic of complexes of transition elements in the Mendeleev table, electronically excited molecules, etc.

Torry: Theory of spin nutation based on Bloch equations

Pumping in resonance

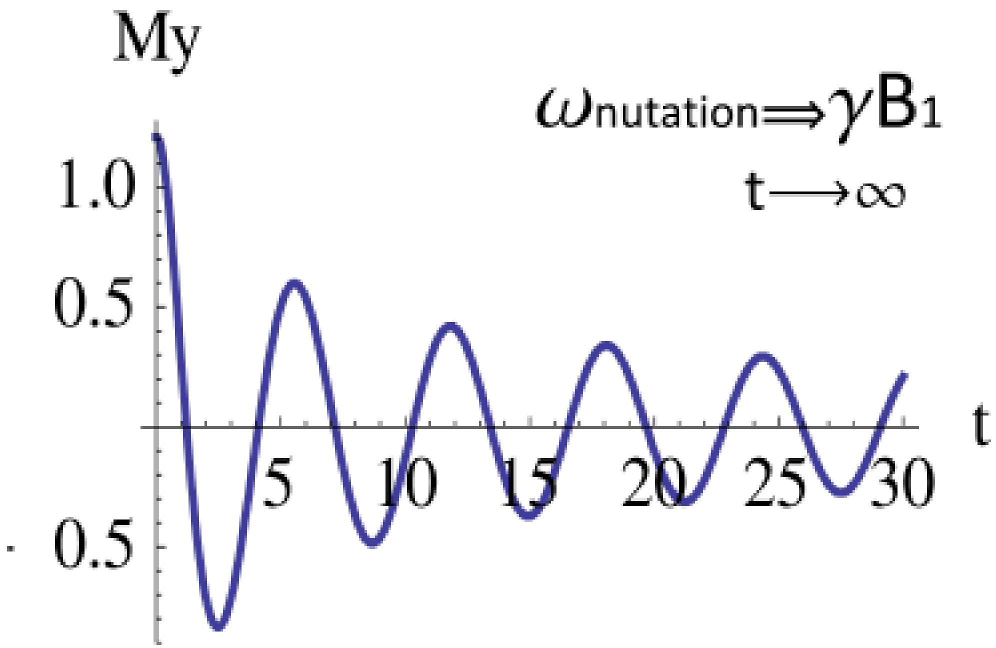
$\omega_1 = \gamma B_1$, nutation frequency



σ=0

Gaussian distribution of ω_0

Pumping at the mean frequency



σ=3

Why quantum spin nutation theory is deviating from theory of Torry?

This deviation is caused by the fact
that in the presence of
spin-spin interactions
the spin dynamics
is not described properly
by Bloch equations

Today I am going to present two quantum description of spin “nutation”, based on Schroedinger and Heisenberg forms of quantum mechanics.

These two approaches ultimately produce the same results. But they make it possible to "visualize" the dynamics of spins in different ways during the experiment.

CONFIRMATION THAT UNDER NON-SELECTIVE EXCITATION of spins nutation does not give information about the value of spin S.

Spin – Hamiltonian in rotating frame

$$H_r = \omega_1 S_x$$

Non-selective excitation of spins.

Operator of the non-selective excitation of spins

$$L = \exp(-i\,\omega_1 S_x t)$$

Nutation frequency equals ω_1 for ANY value of spin S!

Quantum theory of spin nutation:

The change of magnetization of spins with time when the external MW field is suddenly switched on.

A simple example of nutation. Relaxation is neglected.

$H_r = \omega_0 S_z - \omega S_z + \omega_1 S_x$; $\rho(0) = \rho_{eq} = S_z$.

$\rho(t) = \exp(-iH_r t)\, \rho(0)\, (\exp(iH_r t)$;

$My = Tr(S_y \rho(t))$

Possible nutation frequencies are differences $E_{rn} - E_{rm}$,

Possible EPR frequencies in a rotating frame

NON-SELECTIVE EXCITATION

Nutation frequencies for simple model with

$H_r = \omega_0 S_z - \omega S_z + \omega_1 S_x$

For $\omega_0 = \omega$

$H_r = \omega_1 S_x$

In basis of |m>,
the eigen states of S_z, nonzero elements of H_r are equal to
$(H_r)_{m,m-1} = (H_r)_{m-1,m} = (\omega_1/2)\ \{(S+m)(S-m+1)\}^{1/2}$.

Thus transition matrix elements of H_r do depend on m value.

But nutation frequency manifests the difference between eigenvalues of the spin-Hamiltonian H_r.

Those eigenvalues are equidistant energy levels separated by independent on the S value:

$$E_r = \{\omega_1 S,\ \omega_1 (S-1), \ldots, -\omega_1 S\}.$$

Effect of initial state of spins on manifestation of nutation frequencies for simple model with **$H_r = \omega_0 S_z - \omega S_z + \omega_1 S_x$**

$\rho_0 = S_z$

$\rho(t) = \exp(-iH_r t)\, S_z\, (\exp(iH_r t)$; $My = Tr(S_y \rho(t))$

There might be nutation frequencies $\omega_1, 2\omega_1, \ldots, 2\omega_1 S$.

But according to calculations presented above only one frequency, ω_1, appeared.

This the is result of the definite choice of the initial state of spins, $\rho_0 = S_z$, and on observable, S_y, since both operators, S_y and S_z, have only one quantum coherences in the basis of the eigenstates in the simple situation presented in previous slide.

To observe more potentially possible frequencies of nutation one would have to prepare a spin system in the state with, e.g., quadrupolar order and to detect not dipolar but quadrupolar moment.

Frequency selective excitation

of spins in the first approximation of the perturbation theory for the model system, considered on the previous slide

Simple example: $H_r = \omega_0 S_z - \omega S_z + DS_z^2 + \omega_1 S_x$; S=1;

$\omega = \omega_0 + D$;

$$H_r = \begin{matrix} 0 & \omega 1/\sqrt{2} & 0 \\ \omega 1/\sqrt{2} & 0 & \omega 1/\sqrt{2} \\ 0 & \omega 1/\sqrt{2} & 2D \end{matrix}$$

Under chosen conditions 2 energy levels have equal energies (0) and the 3-rd has energy 2D. If $\omega_1 << D$, then in the first order of the perturbation theory

(ω_1 / D<<1)

$$H_r \approx \begin{matrix} 0 & \omega_1/\sqrt{2} & 0 \\ \omega_1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 2D \end{matrix}$$

Selective excitation of spins in the first approximation of the perturbation theory for the model system, considered on previous slide

Thus, in this approximation only one (1⇔2) transition is selectively excited and nutation frequency equals $\sqrt{2}\,\omega_1$ instead of being equal to ω_1 in the case of nonselective approximation.

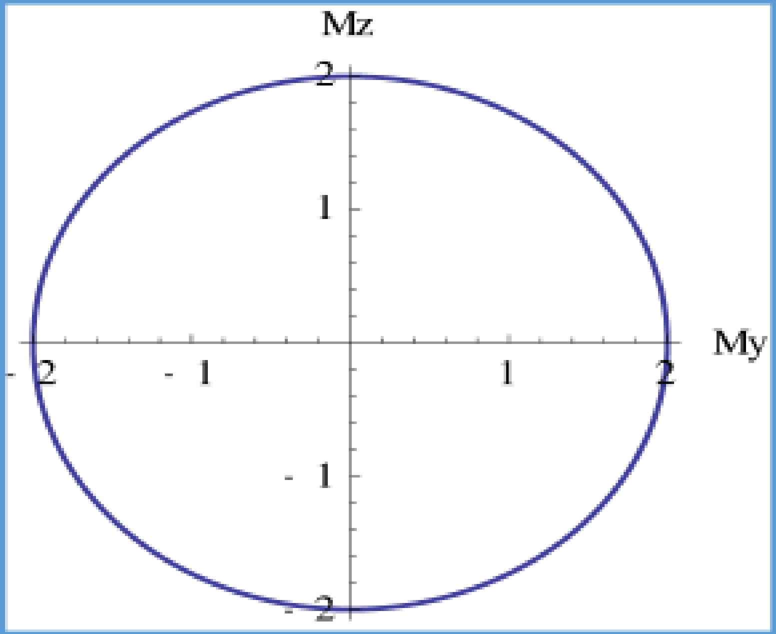
If $\omega=\omega_0$-D, then only one (2⇔3) transition is selectively excited and nutation frequency equals again $\sqrt{2}\,\omega_1$

Nutation of spins S=1 for limited cases of excitation

Curves are calculated for $\omega 1=1$ Gs

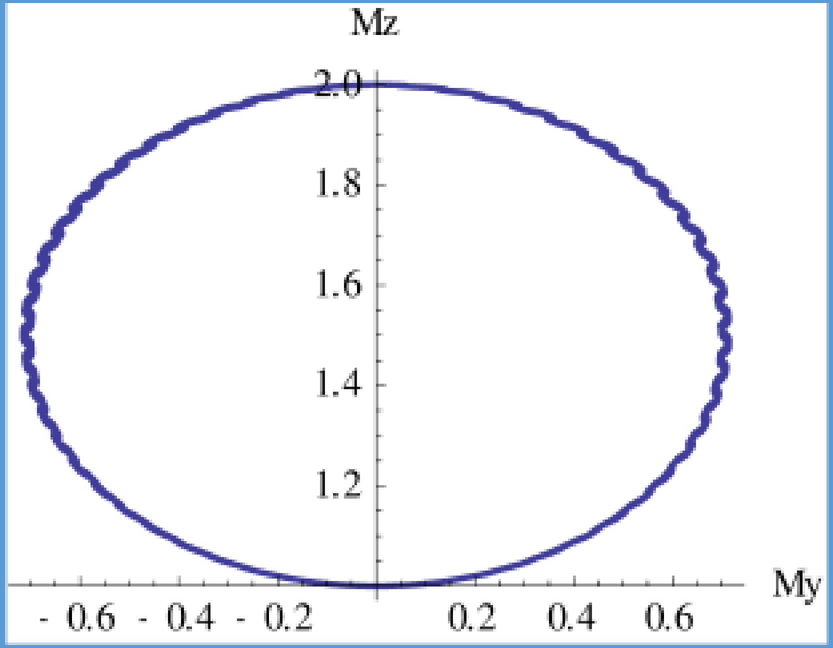
Nonselective excitation

D=0



Frequency selective excitation

D=30 Гс, $\omega=\omega 0+D$

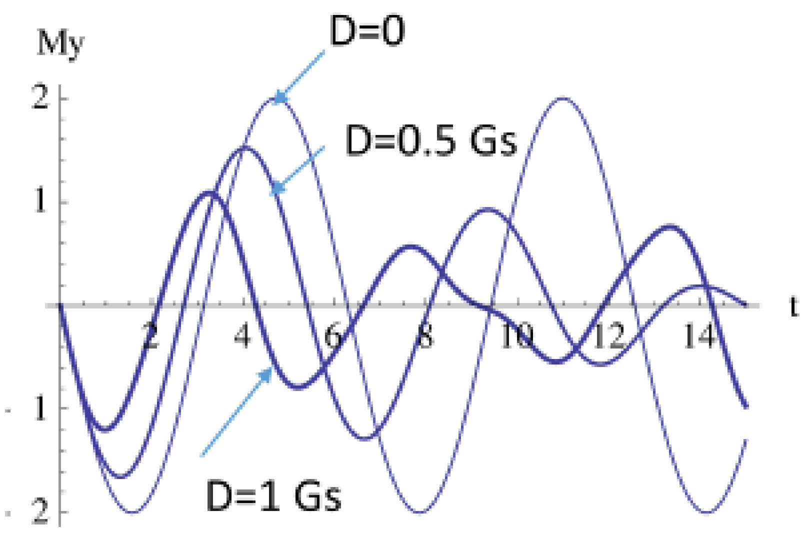


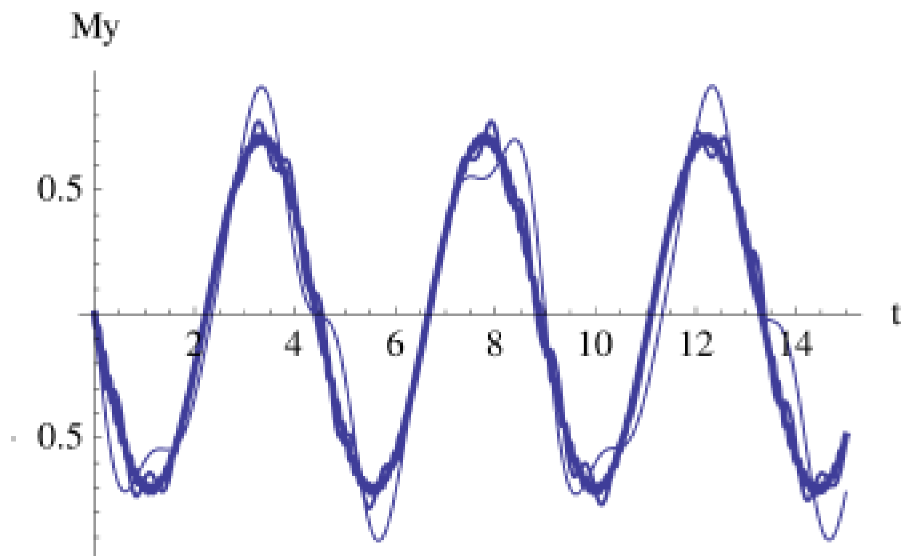
Selective excitation of spins in a general case for the model system

$$H_r = \begin{matrix} 0 & \omega 1/\sqrt{2} & 0 \\ \omega 1/\sqrt{2} & 0 & \omega 1/\sqrt{2} \\ 0 & \omega 1/\sqrt{2} & 2D \end{matrix}$$

For the spins
with S=1 and the spin-Hamiltonian presented above
the nutation was numerically calculated
using the theoretical expression
$M_y = Tr\{S_y \exp(-iH_r t)\, S_z (\exp(iH_r t)\}$.

Selective excitation of spins in a general case for the model system.
D=0 corresponds to non-selective excitation of spins



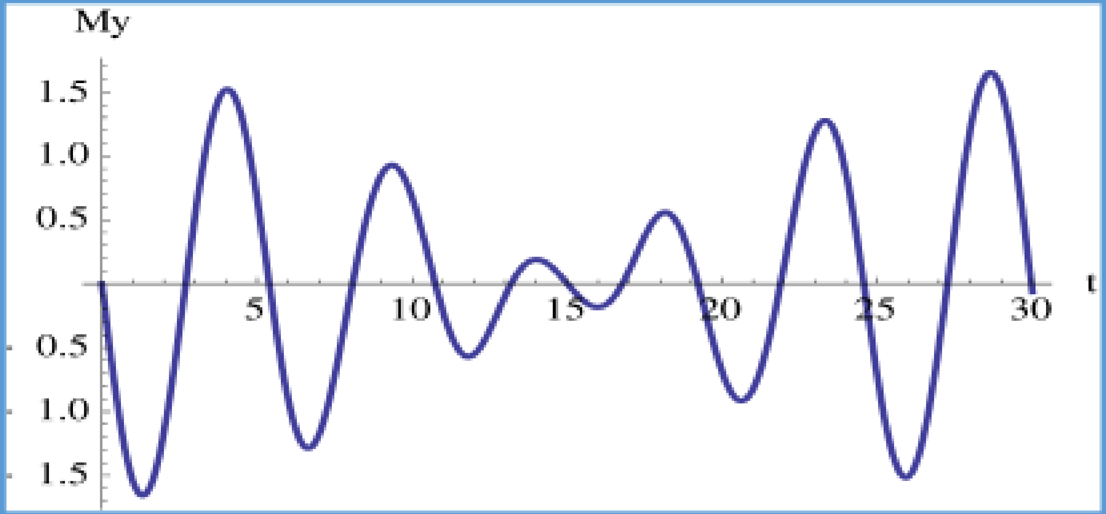


Parameters: ω_1 = 1 Gs, Left curves, D=0, 0.5 Gs, 1Gs.
Thickness of curves increases with increasing D.

With increasing D the nutation frequency shifts from ω_1 to $\sqrt{2}\,\omega_1$.

Right curves, D=2 Gs, % Gs, 10 Gs, 30 G.
Nutation frequency does not change practically and equals to $\sqrt{2}\,\omega_1$.

Curve from previous slide, D=0.5 Gs



$$My = -0.76 \mathrm{Sin}(1.05t) - 0.9 \mathrm{Sin}(1.25t) - 0.024 \mathrm{Sin}(2.3t).$$

What information
can be obtained from
nutation EPR experiment?

Frequencies determined when nutation is observed.

EPR in rotating frame?

$\rho(t)=\exp(-iH_r t)\ \rho(0)\ (\exp(iH_r t)$

In basis of the H_r eigenstates any oscillations of an observed signal are determined by the spin coherences

$\rho_{kn}(t)= \rho_{kn}(0)\exp(-i\ \Delta_{kn})t),\ \Delta_{kn}=(E_r)_k-(E_r)_n.$

Contributions of terms with different frequencies Δ_{kn} depend on $\rho_{kn}(0)$ and observable Q. Note in Torry case $Q=S_y$

What is today quantum spin nutation theory?

There are numerous examples of quantum calculations of spin moment motion after sudden switching on of alternating magnetic fields.

Results:

When excitation of spins happens to be
the really non-selective and
the initial state of spin can be described as $\rho_0 = S_z$
we obtain Torry results for nutation

What is today quantum spin nutation theory?

When only one resonance transition is excited by
the alternating field we obtain Torry-type nutation with
the frequency of nutation depending on the value of spin S.

What is today quantum spin nutation theory?

When spin-spin interaction is comparable with the interaction of spins with alternating field B1 then a motion of magnetization vector is not nutation.

There are manifested several oscillating contributions to the observed signal.

What is today quantum spin nutation theory?

When spin-spin interaction is comparable
with the interaction of spins with alternating field B1
the module of the magnetic moment
is changing essentially with time.

Why quantum spin nutation theory is deviating from theory of Torry?

This deviation is caused by the fact
that in the presence of
spin-spin interactions
the spin dynamics
is not described properly
by Bloch equations

Why Bloch equations appear to be not applicable for describing spin dynamics in general case?

Bloch equations assumes that the magnetization (dipole moment) of spin provides full description of the spin state.

But this is true
only for particles with S=1/2.

Therefore Torry nutation theory is valid only for non-interacting particles with spin S=1/2.

How do we describe the spin states

For the case S=1, full description of the spin state is given by its dipole and quadrupole moments:

```
Fx=(1/Sqrt[2]) {{0,1,0},{1,0,1},{0,1,0}};

Fy=(1/Sqrt[2]) {{0,-I,0},{I,0,-I},{0,I,0}};

Fz={{1,0,0},{0,0,0},{0,0,-1}};

E={{1,0,0},{0,1,0},{0,0,1}};

Fxxyy=Fx.Fx-Fy.Fy;

Fzz=Fz.Fz-(2/3) FF;

Fxy=Fx.Fy+Fy.Fx;

Fxz=Fx.Fz+Fz.Fx;

Fyz=Fy.Fz+Fz.Fy;
```

Coupled equations of the first derivatives of observables

Simple equation of "nutation" of S=1.

$H_r = \omega_0 S_z - \omega S_z + D\, Sz\hat{}2 + \omega_1 S_x$; $\rho(0) = \rho_{eq} = S_z$.

$\partial \mathbf{S}_x/\partial t = D\, \mathbf{S}_y - D\, \mathbf{Q}_{yz}$;

$\partial \mathbf{S}_y/\partial t = -D\, \mathbf{S}_x - \omega_1 \mathbf{S}_z + D\, \mathbf{Q}_{xz}$;

$\partial \mathbf{S}_z/\partial t = \omega_1 \mathbf{S}_y$;

$\partial \mathbf{Q}_{xy}/\partial t = -2\, D\, \mathbf{Q}_{xxyy} - \omega_1 \mathbf{Q}_{xz}$;

$\partial \mathbf{Q}_{xz}/\partial t = -D\, \mathbf{S}_y + \omega_1 \mathbf{Q}_{xy} + D\, \mathbf{Q}_{yz}$; (3)

$\partial \mathbf{Q}_{yz}/\partial t = D\, \mathbf{S}_x - \omega_1 \mathbf{Q}_{xxyy} - 3\, \omega_1 \mathbf{Q}_{zz} - D\, \mathbf{Q}_{xz}$;

$\partial \mathbf{Q}_{zz}/\partial t = \omega_1 \mathbf{Q}_{yz}$;

$\partial \mathbf{Q}_{xxyy}/\partial t = 2\, D\, \mathbf{Q}_{xy} + \omega_1 \mathbf{Q}_{yz}$.

For t=0 only one variable is non-zero
when Eq.(6) case operates: Fz(0)=2

Coupled equations of second derivatives of observables

Simple example of “nutation” of S=1.

$H_r = \omega_0 S_z - \omega S_z + D\, Sz\verb|^|2 + \omega_1 S_x$; $\rho(0) = \rho_{eq} = S_z$.

```
Fx''=D(2D(-Fx+Fxz)+(Fxxyy-Fz+3Fzz)w1),                (D Sqrt[2])
Fy''=2D²(-Fy+Fyz)+Fxy Dw1-Fy w1²,                     (Sqrt[w1^2+2D^2])
Fz''=-w1(D(Fx-Fxz)+Fzw1),                             (w1)
Fxxyy''=-4D² Fxxyy+Dw1(Fx-3 Fxz)-(Fxxyy+3Fzz) w1²,    (Sqrt[w1^2+4D^2])
Fzz''=-w1(D(-Fx+Fxz)+(Fxxyy+3Fzz) w1),               w1 Sqrt[3])
Fxy''=-4D² Fxy+Dw1(Fy-3Fyz)-Fxy w1²,                  (Sqrt[w1^2+4D^2])
Fxz''=2D²(Fx-Fxz)+Dw1(-3Fxxyy+Fz-3Fzz)-Fxz w1²        (Sqrt[w1^2+2D^2])
Fyz''=2D²(Fy-Fyz)-3Dw1 Fxy-4FyzD w1².                 (Sqrt[4w1^2+2D^2])
```

For t=0 and Eq.(6) there are in thermal equilibrium two non-zero variables only: Fz(0)=2, Fy'(0)=-2 w1.

Equations for limit cases

$\omega 1=0$

$Fx''=2D^2(-Fx+Fxz)$,

$Fy''=2D^2(-Fy+Fyz)$,

$Fz''=0$,

$Fxxyy''=-4D^2\ Fxxyy$,

$Fzz''=0$,

$Fxy''=-4D^2\ Fxy$

$Fxz''=2D^2(Fx-Fxz)$,

$Fyz''=2D^2(Fy-Fyz)$.

$D=0$

$Fx''=0$,

$Fy''=-Fy\ w1^2$,

$Fz''=-Fz\ w1^2$,

$Fxxyy''=-(Fxxyy+3Fzz)\ w1^2$,

$Fzz''=-(Fxxyy+3Fzz)\ w1^2)$,

$Fxy''=-Fxy\ w1^2$,

$Fxz''=-Fxz\ w1^2$

$Fyz''=-4Fyz\ w1^2$.

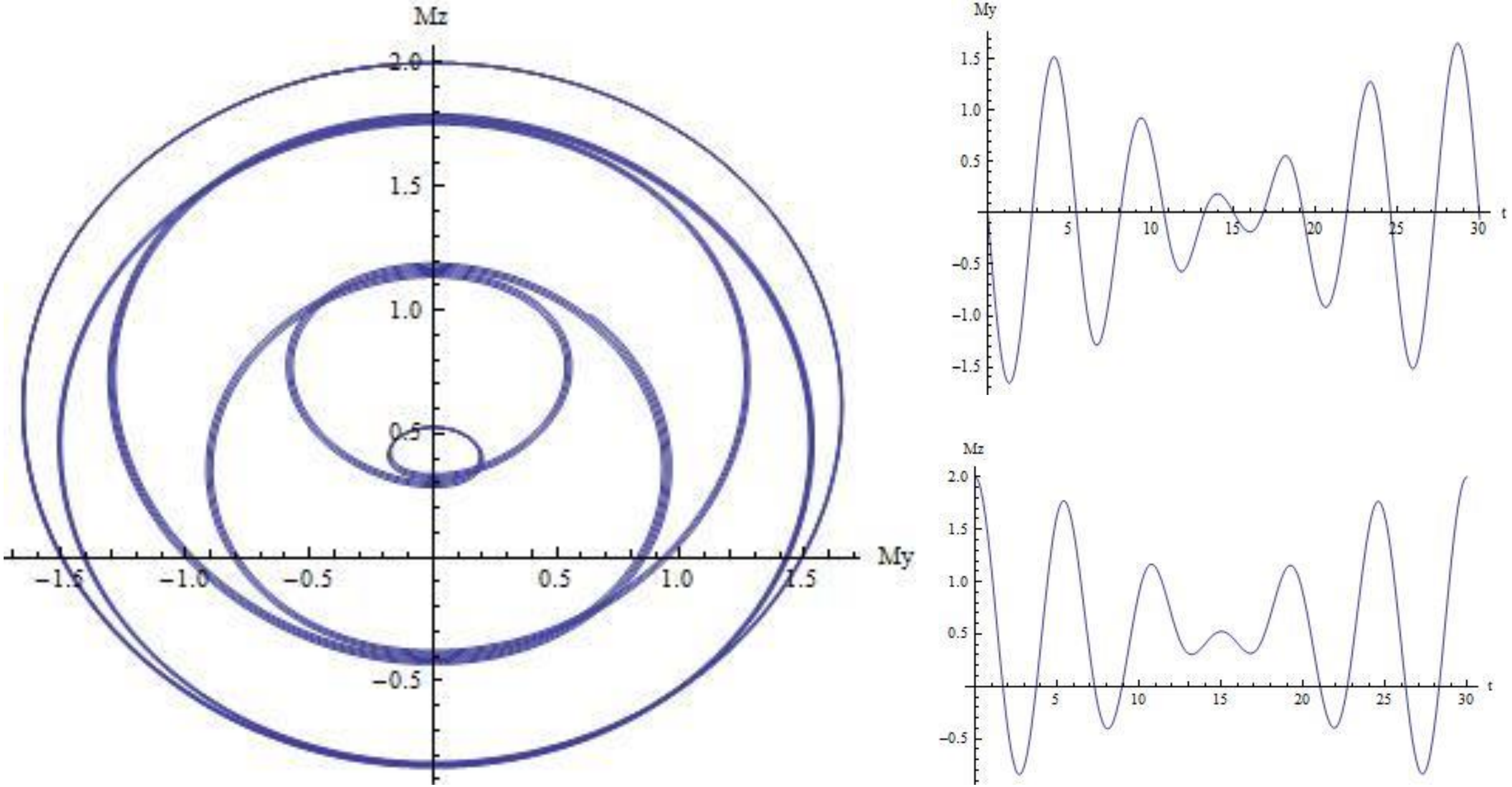
Time dependence of dipole moment projections

$\omega 1=1$ Gs,

D=1 Gs,

$\omega=\omega_0+D$

My, Mz



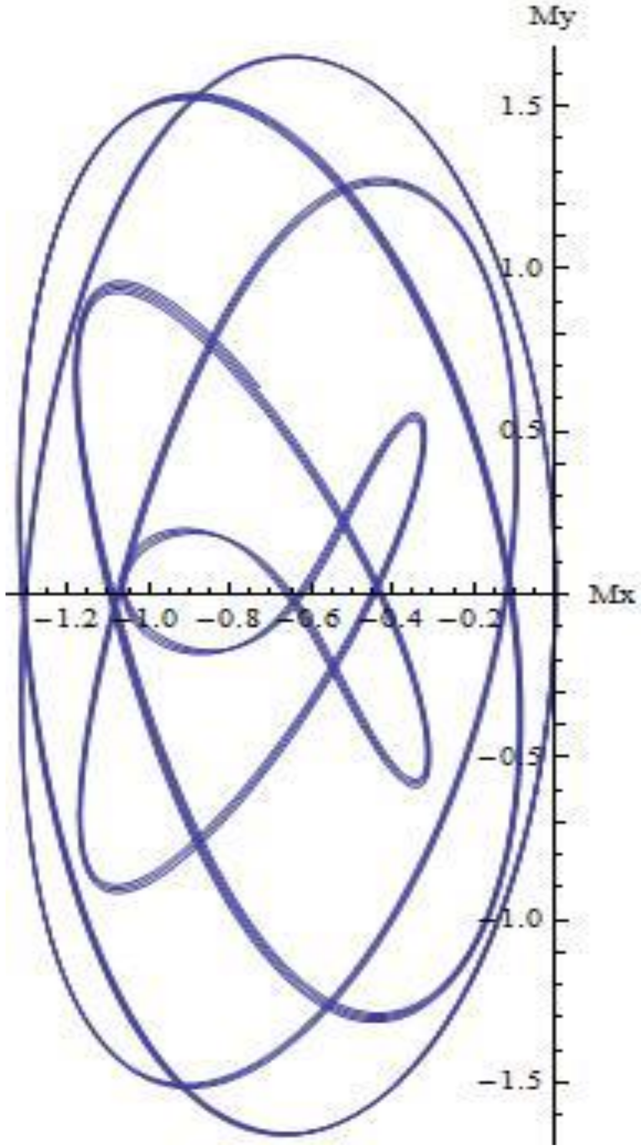
Time dependence of dipole moment projections

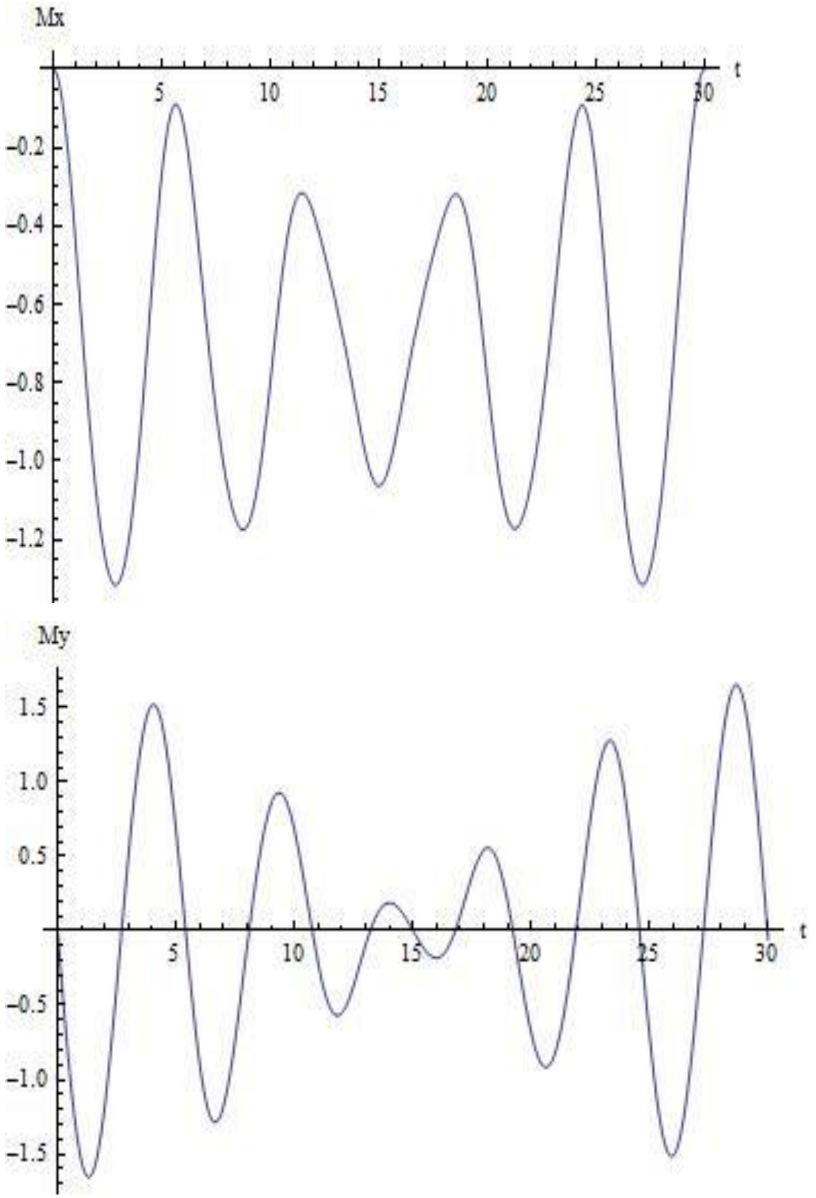
ω_1=1 Gs,

D=1 Gs,

$\omega=\omega_0$+D

Mx, My



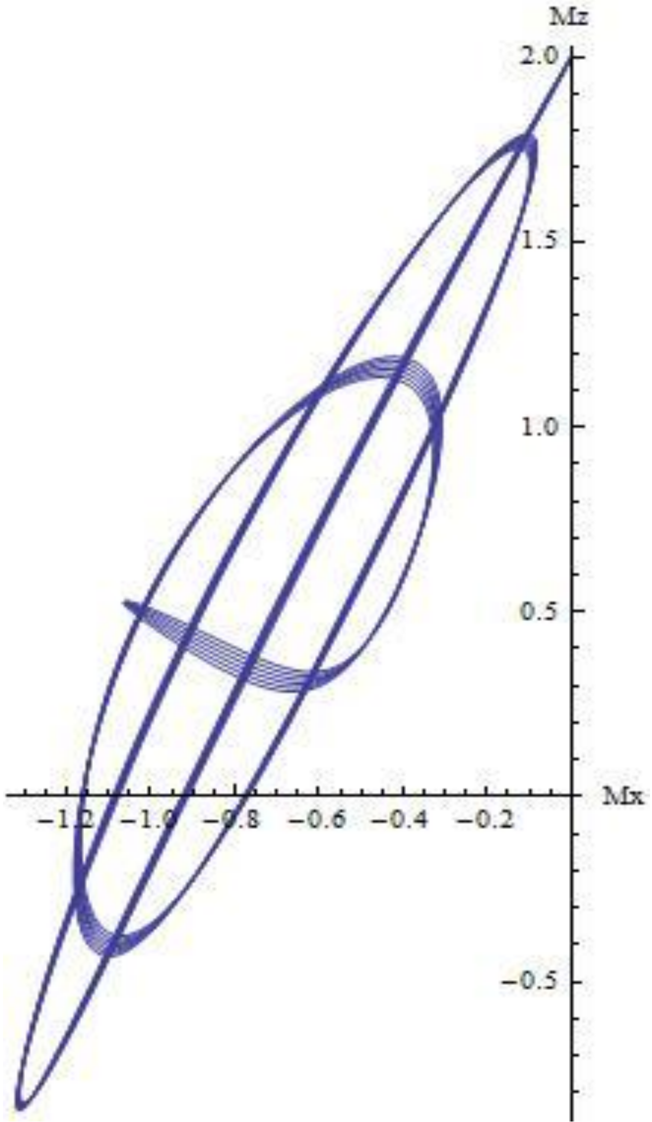


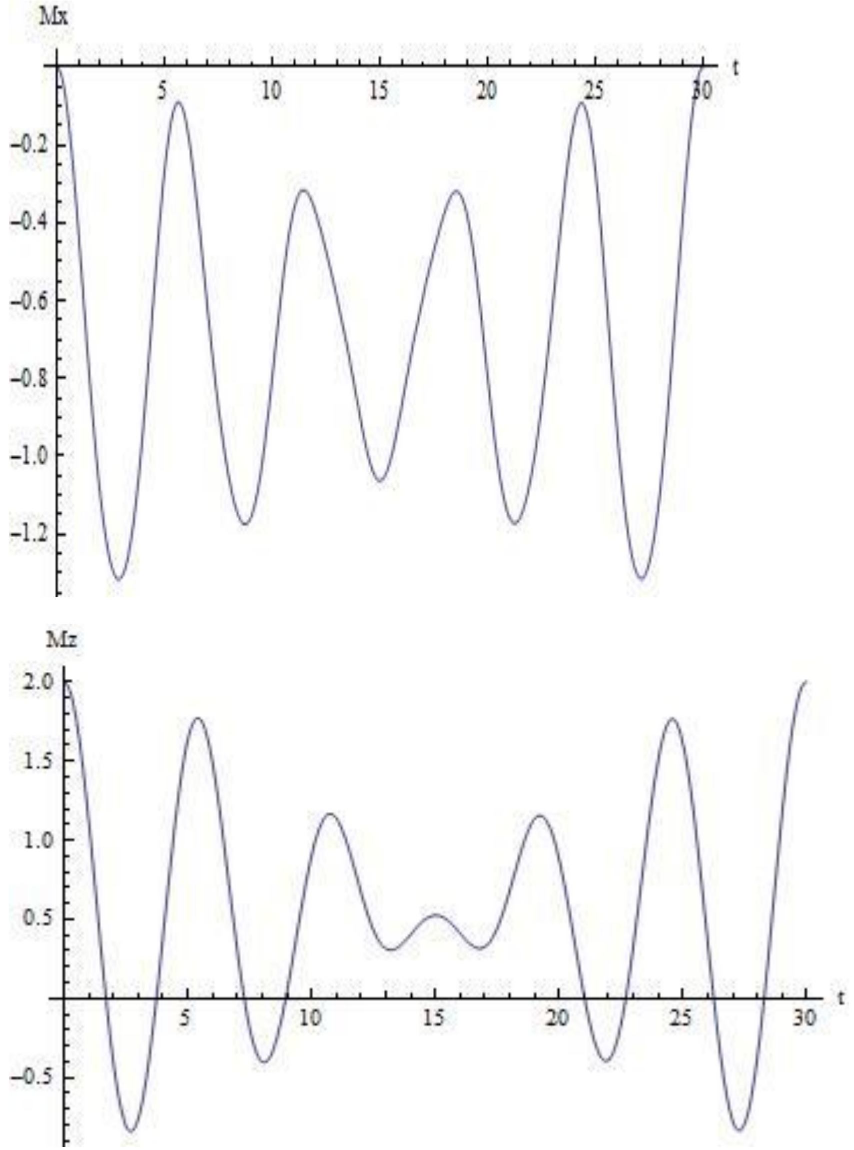
Mx, Mz

Time dependence of quadrupole components

ω_1=1 Gs, D=1 Gs,

$\omega=\omega_0$+D



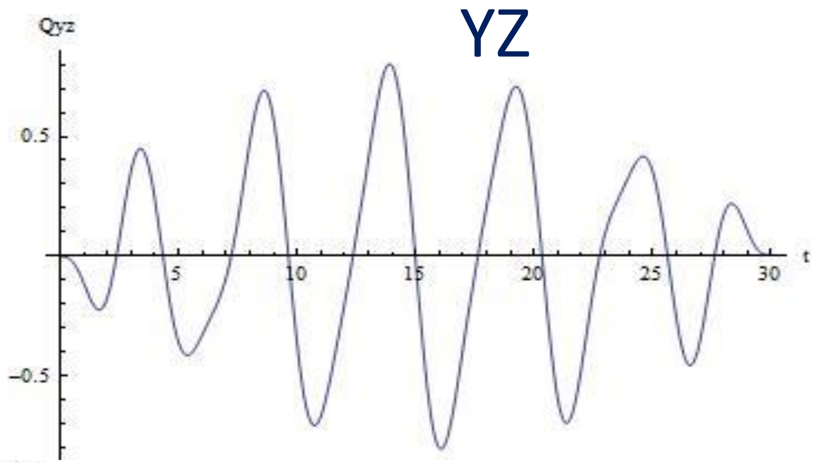


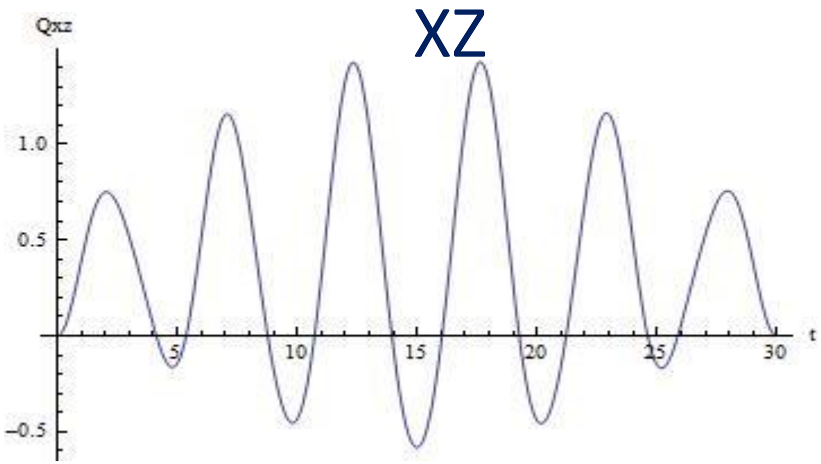
Time dependence of quadrupole components:

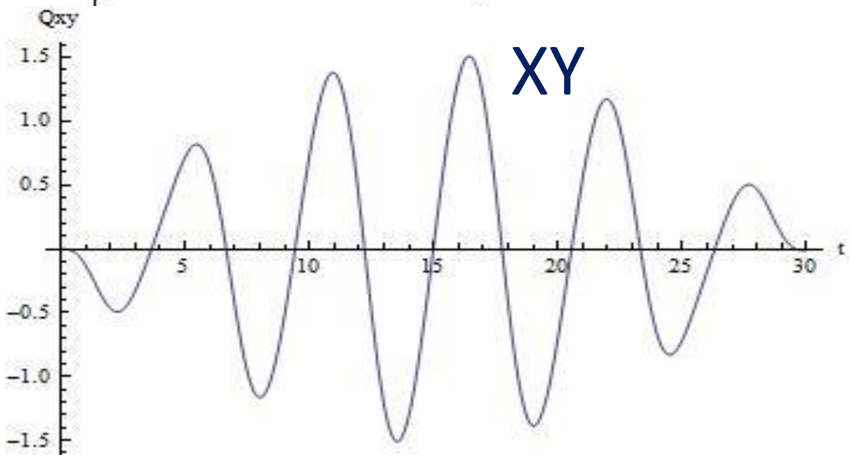
ω1= Gs,

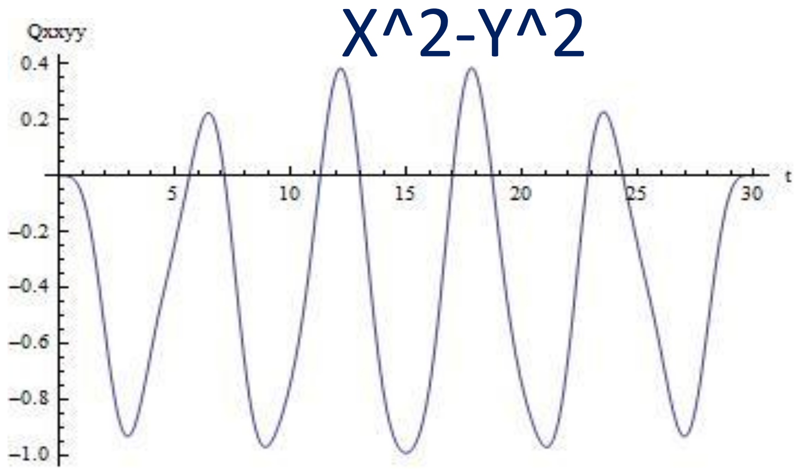
D=1 Gs,

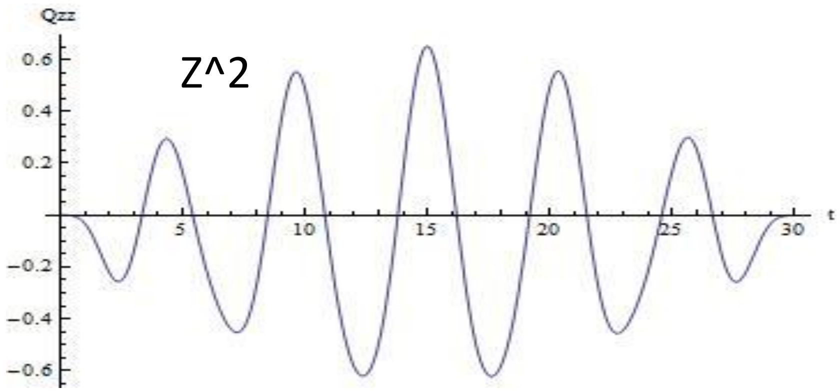
$\omega=\omega_0$+D











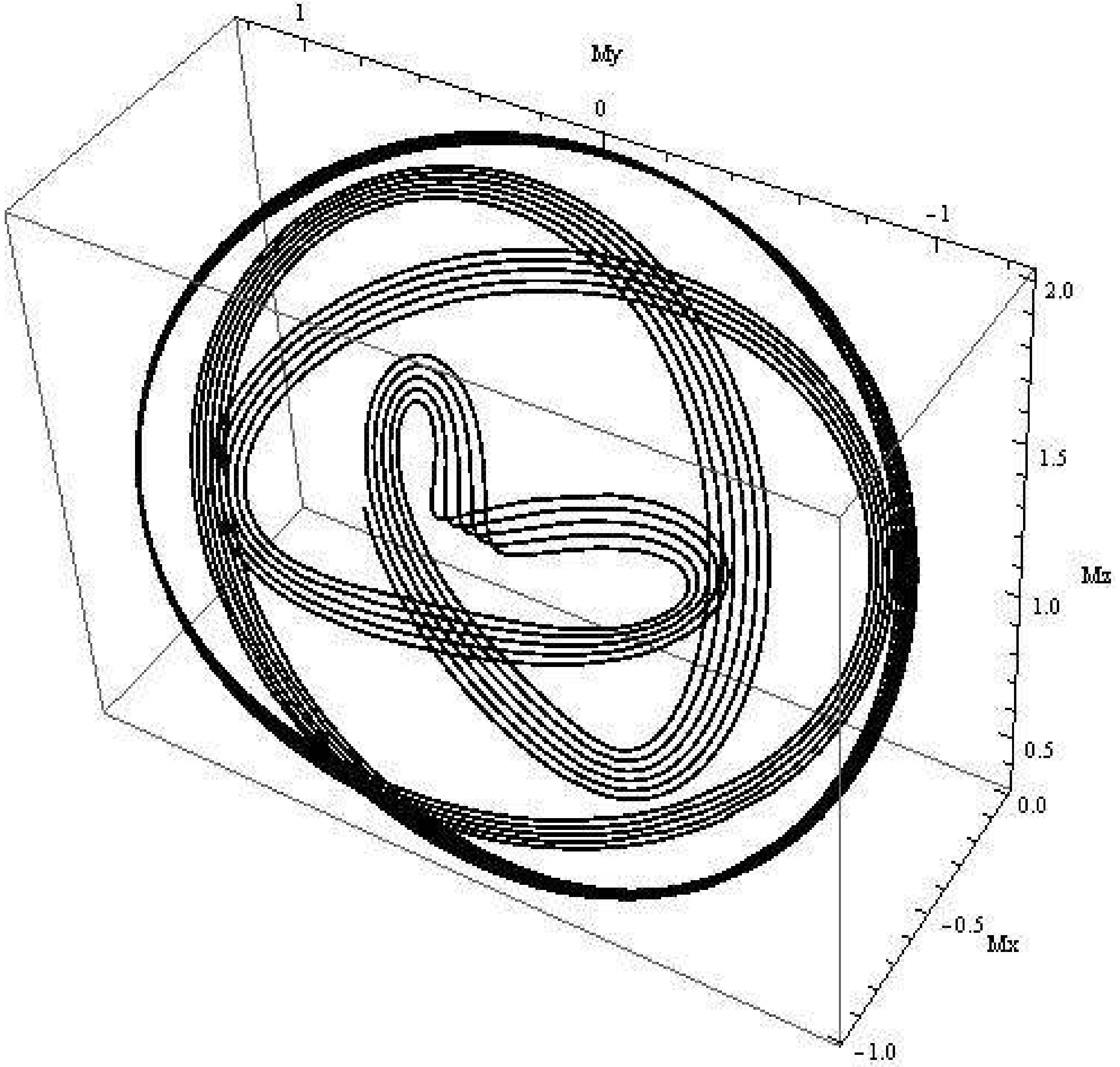
3D picture of the dipole moment motion

ω_1= Gs,

D=1 Gs,

$\omega=\omega_0+D$,

t_{max}=130



Conclusions

- The “nutation” of the dipole moment of spins, taking into account the spin-spin interaction, cannot be reduced to Torrey nutation, in principle.
- “Nutation” of spins in the presence of spin-spin interaction cannot be understood without taking into account the multipole moments of spins.
- For the spin S=1, a system of coupled linear differential equations for the projections of the dipole magnetic moment and the components of the quadrupole magnetic moment is obtained explicitly.
- The Bloch equations cannot be used to describe the "nutation" of interacting spins (including the splitting of spin energy levels in a zero magnetic field).

1. Current state of the theory makes it possible to use nutation method to get all magnetic resonance parameters: spin Hamiltonian parameters, paramagnetic relaxation times and the value of spins.
2. Nutation allows to study photoinduced hyperpolarization of spins (S. Weissmann)
3. Nutation experiments can be implemented on a base of steady state EPR spectrometers.

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THANK YOU

FOR YOUR ATTENTION