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Model of the water signal shape from the Bloch equations

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Abstract

We present here a model of the water signal shape that can be used to fit the water data in order to calibrate the NMR polarization measurement system.

1 The Bloch Equations

The Bloch equations describe the time evolution of the water sample nuclear magnetization $\vec{M}$, defined as the magnetic momentum of the sample per unit of volume (IS unit : Ampere per meter). The Bloch equations in the rotating frame ($\hat{x}$,$\hat{y}$,$\hat{z}$), when a d.c. field $\vec{H}$ is applied along the $\hat{z}$ axis, and a r.f. field $\vec{H_1}$ always aligned in the direction of the $\hat{x}$ axis and rotating around the $\hat{z}$ axis, are written as :

$$\begin{aligned}
\frac{dM_x}{dt} &= -\frac{(M_x - \chi_0 H_1)}{T_2} + \Delta\omega M_y && (1)\\
\frac{dM_y}{dt} &= -\Delta\omega M_x - \frac{1}{T_2} M_y - \omega_1 M_z && (2)\\
\frac{dM_z}{dt} &= -\omega_1 M_y - \frac{(M_z - M_0)}{T_1} && (3)
\end{aligned}$$

using the definitions of [1] and assuming H and H_1 are of the same order of magnitude. In our case, these equations can be applied to the water sample macroscopic polarization vector $\vec{P}$ which is unitless :

$$\begin{aligned}
\frac{dP_x}{dt}(t) &= -\frac{1}{T_2} P_x(t) + \gamma[H(t) - H_0] P_y(t) + \frac{1}{T_2}\chi H_1 && (4)\\
\frac{dP_y}{dt}(t) &= -\gamma[H(t) - H_0] P_x(t) - \frac{1}{T_2} P_y(t) + \gamma H_1 P_z(t) && (5)\\
\frac{dP_z}{dt}(t) &= -\gamma H_1 P_y(t) - \frac{1}{T_1} P_z(t) + \frac{1}{T_1}\chi H(t) && (6)
\end{aligned}$$

with the following definitions, using Gauss (G) instead of Tesla (T) for the magnetic field unit :

- T_2 : transverse relaxation time, in s
- γ : gyromagnetic ratio of the proton, $\gamma = 2.67515255.10^4$ s^{-1} G^{-1}
- H : component along $\hat{z}$ of the effective holding field $\vec{H_{eff}}$
- H_0 : resonance field, $H_0 = 2\pi f/\gamma = 21.37$ G, where the RF frequency is $f = 91$ kHz
- α : ramping speed of the holding field along the $\hat{z}$ axis, $\alpha = 1.2$ G.s^{-1} and $H(t) = H_0 + \alpha t$
- χ : ratio $\mu_{p,H_2O}/kT$, where $\mu_{p,H_2O} = 1.4106089.10^{-26}$ JT^{-1} is the magnetic momentum of protons in water, k is the Boltzman constant (in JK^{-1}) and T is the temperature (in K). Note that the thermal polarization of water is given by : $P = tanh(\chi H) \simeq \chi H$. Numerically, $\chi = 3.4616068.10^{-10}$ G^{-1} at 22 ^{o}C

- H_1 : RF field at $f = 91$ kHz, in G. Then, in the rotating frame, $\vec{H_{eff}} = H_1\hat{x}+(H-H_0)\hat{z}$. For our setup, we have measured $H_1 = 72.83$ mG.
- T_1 : longitudinal relaxation time, in s

2 Numerical Integration

It is not possible to find an analytical solution to the previous differential system. However, we can find a numerical solution, using for example the Mathematica 3.0© software. For the results shown below, we have assumed $T_1 = T_2 = 2$ s. The d.c. field H generated by the Helmholtz coils is swept from 18 G to 25 G, along the $\hat{z}$ axis. To solve numerically the first order differential equations, we need to specify the initial value of each of the three components of the polarization when the sweep starts, at the time t_i. To calculate these three values, we simply solve the Bloch system, requiring each first derivative to be zero at t_i :

$$
\begin{aligned}
\frac{dP_x}{dt}(t=t_i) &= 0 = -\frac{1}{T_2}P_x(t_i) + \gamma[\alpha t_i]P_y(t_i) + \frac{1}{T_2}\chi H_1 &(7)\\
\frac{dP_y}{dt}(t=t_i) &= 0 = -\gamma[\alpha t_i]P_x(t_i) - \frac{1}{T_2}P_y(t_i) + \gamma H_1 P_z(t_i) &(8)\\
\frac{dP_z}{dt}(t=t_i) &= 0 = -\gamma H_1 P_y(t_i) - \frac{1}{T_1}P_z(t_i) + \frac{1}{T_1}\chi[H_0 + \alpha t_i] &(9)
\end{aligned}
$$

The initial time t_i is negative : $t_i = -(H_{max} - H_{min})/2\alpha \simeq -2.92$ s and corresponds to $H = H_{min} = 18$ G ; the $\hat{z}$ component $H - H_0$ is negative. The resonance is assumed to occur at $t = 0$, where $H = H_0$ and $H_{eff} = H_1$, and the sweep stops at $t_f = -t_i$, when $H = H_{max} = 25$ G ; the $\hat{z}$ component $H - H_0$ is positive.

Mathematica 3.0© gives us the numerical solutions :

$$
\begin{aligned}
P_x(t_i) &= -1.28653.10^{-10} &(10)\\
P_y(t_i) &= 8.21656.10^{-16} &(11)\\
P_z(t_i) &= 6.18269.10^{-9} &(12)
\end{aligned}
$$

With those initial conditions, we can integrate numerically the system of differential equations. To compare with the following section we have chosen $T_1 = T_2 = 2$ s.

3 Analytical Solution

It is possible to reduce the system to one equation only, assuming the equality $T_1 = T_2$. In that case, the polarization of the sample remains always aligned with the effective holding

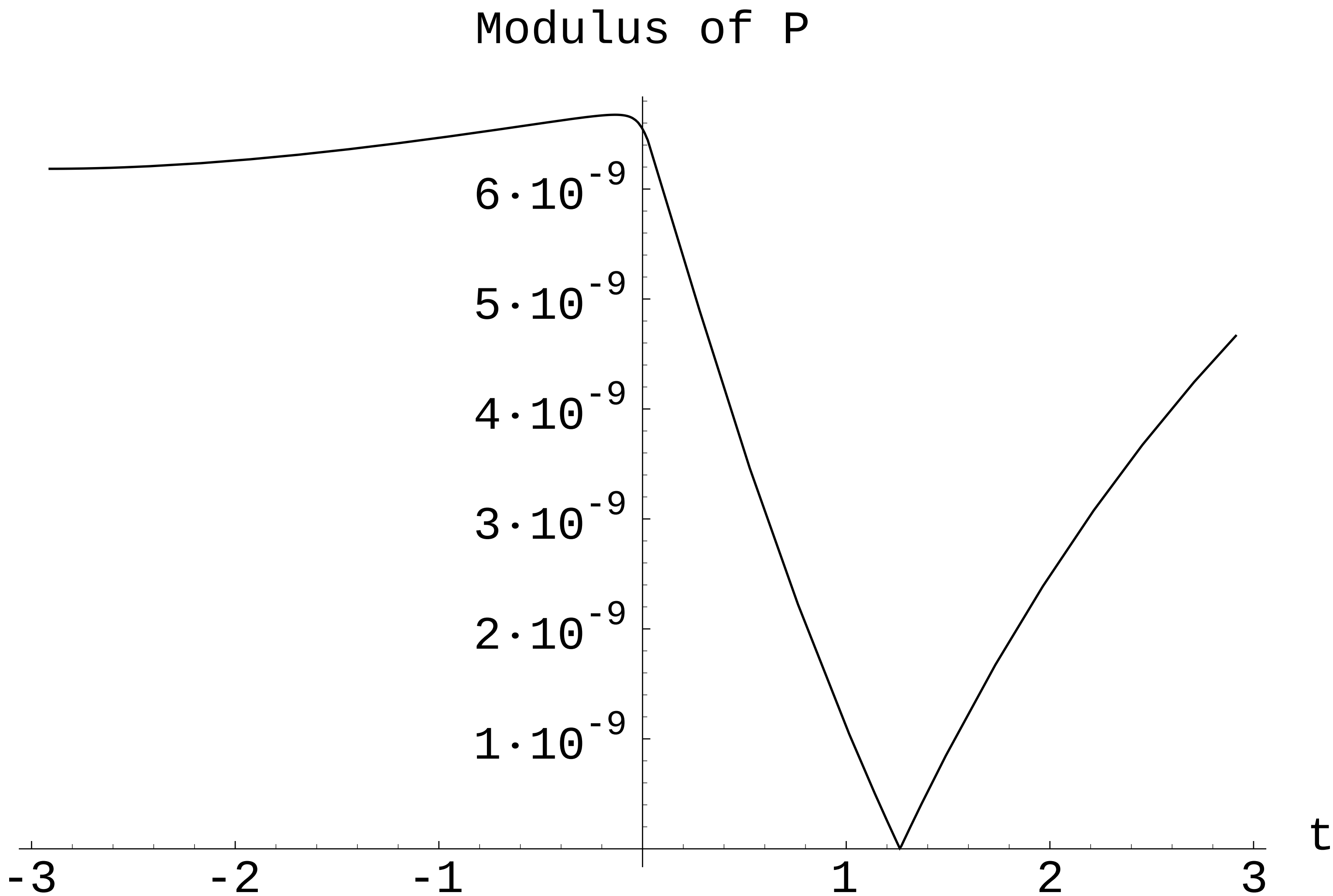

Figure 1: Modulus of the polarization P as a function of time. The modulus goes clearly to zero after the resonance.

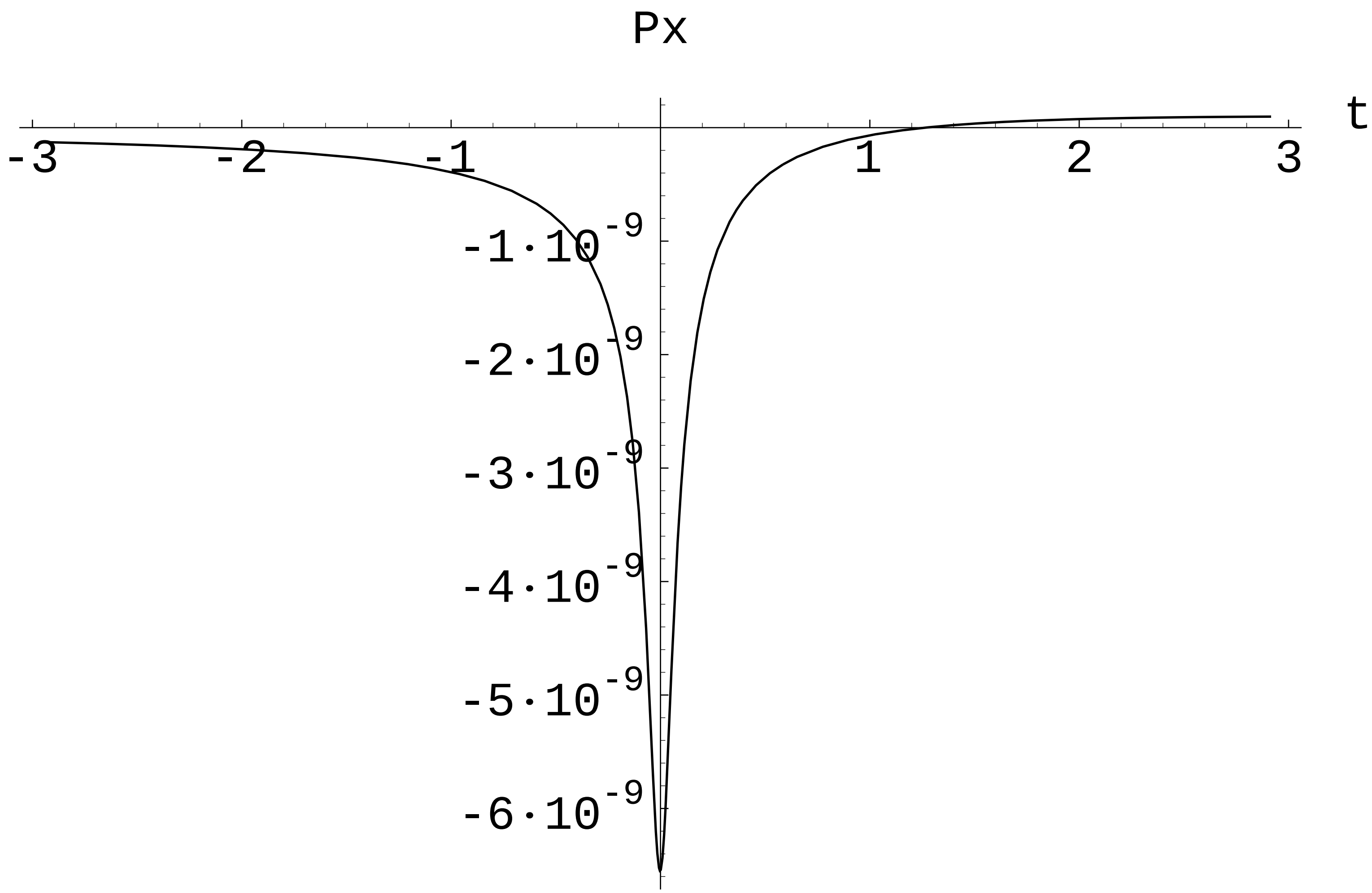

Figure 2: Component P_x of the polarization P as a function of time. This curve is the shape of the water signal detected by the pick-up coils. Note the strong asymmetry of the shape of the water signal.

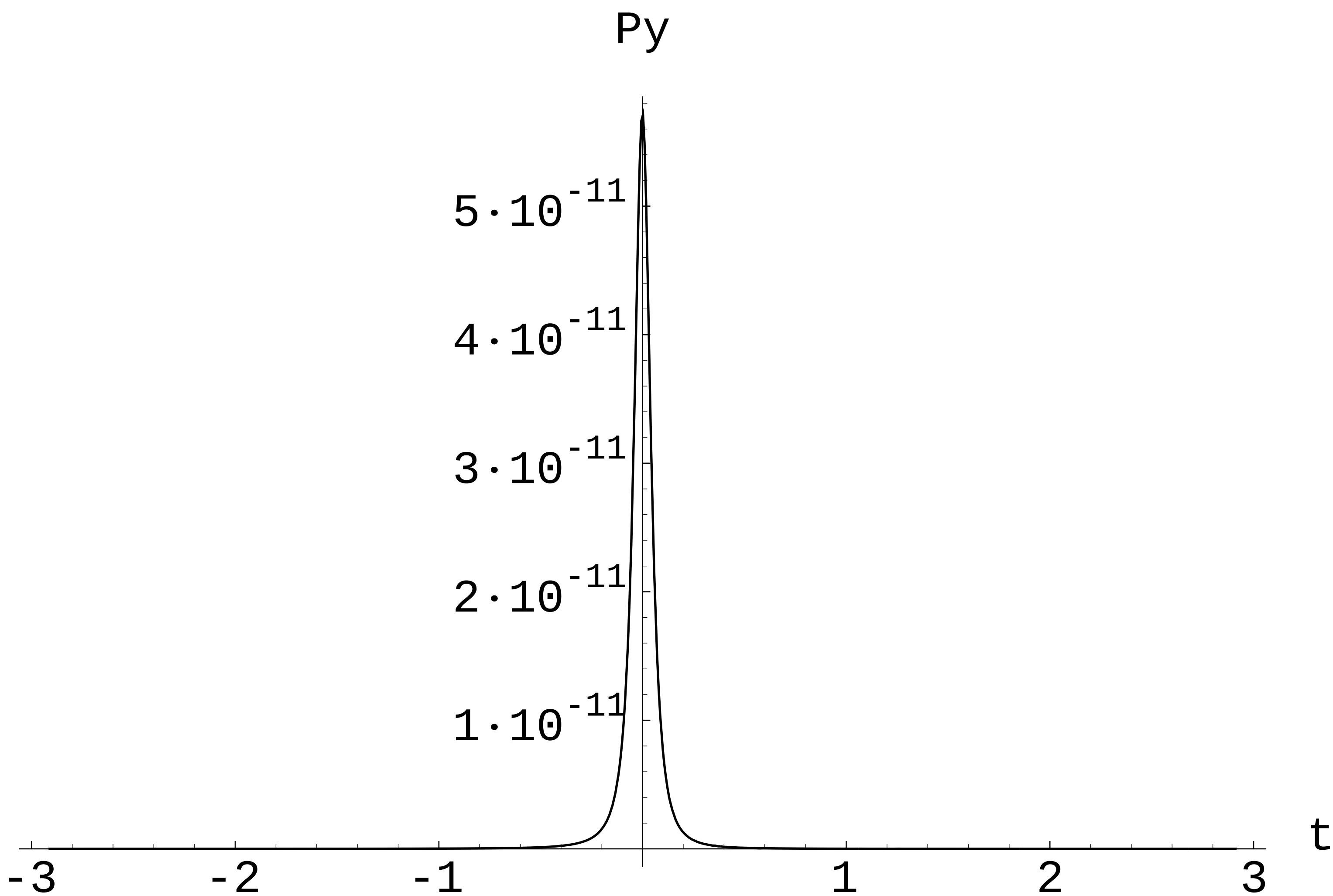

Figure 3: Component P_y of the polarization P as a function of time. The y component is much smaller than the two other components P_x and P_z.

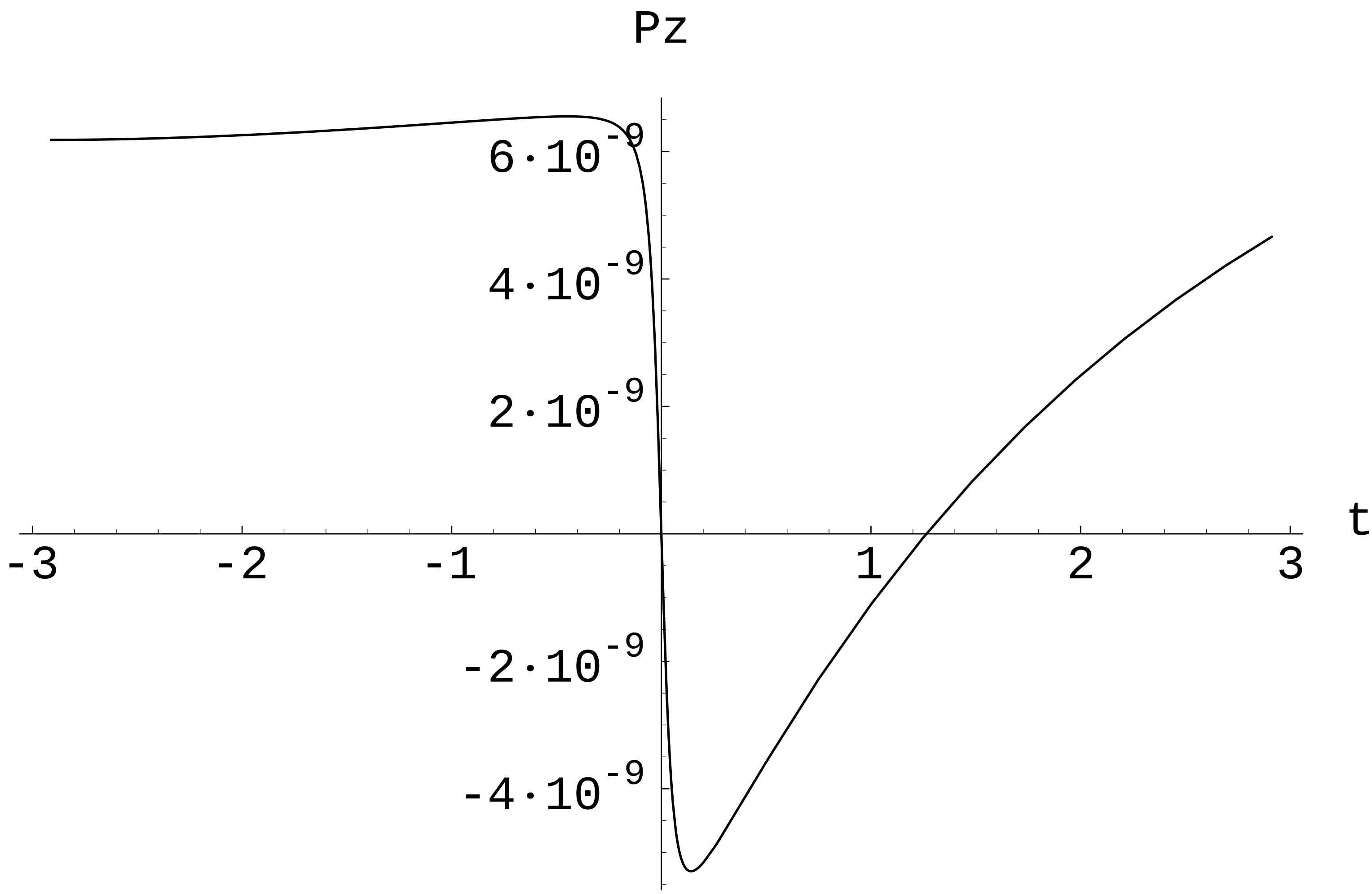

Figure 4: Component P_z of the polarization P as a function of time. When the sweep starts, the magnetization of the water is directed toward the positive direction of the $\hat{z}$ axis. The $\hat{z}$ component is zero at the resonance and is flipped shortly after. The spins are in the high energy state, then they immediately start to flip back to the low energy state. At the end of the sweep, their orientation is close to the one they had before the sweep.

field $\vec{H_{eff}}$ in the rotating frame, [1]. For that purpose, we define the effective polarization of the water sample, P_{eff}, which represents the component of the polarization along the $H_1\hat{x} + (H - H_0)\hat{z}$ direction :

$$P_{eff} = k\sqrt{P_x^2 + P_y^2 + P_z^2} \tag{13}$$

where $k = \pm 1$. Using :

$$\frac{dP_{eff}}{dt} = \frac{P_x\dot{P}_x + P_y\dot{P}_y + P_z\dot{P}_z}{P_{eff}} \tag{14}$$

we get the first order differential equation :

$$\frac{dP_{eff}}{dt}(t) = \frac{1}{T_1}[P_{eff}(t) - P_{eq}(t)] \tag{15}$$

where $P_{eq}(t)$ is defined by :

$$P_{eq}(t) = \chi\frac{H_1^2 + \alpha t(H_0 + \alpha t)}{\sqrt{H_1^2 + \alpha^2 t^2}} \tag{16}$$

and where we have used the following relation, as illustrated on the animation (Figure 9) :

$$\frac{P_x}{P_{eff}} = \frac{H_1}{\sqrt{H_1^2 + \alpha^2 t^2}} \tag{17}$$

$$\frac{P_z}{P_{eff}} = \frac{\alpha t}{\sqrt{H_1^2 + \alpha^2 t^2}} \tag{18}$$

This differential equation can be integrated numerically. The initial condition required is simply given by assuming $\frac{dP_{eff}}{dt}(t = t_i) = 0$, which leads to : $P_{eff}(t_i) = P_{eq}(t_i)$.

The solution of the differential equation in the integral form is given by :

$$P_{eff}(t) = e^{-(t-t_i)/T_1}\left[P_{eq}(t_i) + \frac{1}{T_1}\int_{t_i}^{t} e^{(u-t_i)/T_1}P_{eq}(u)du\right] \tag{19}$$

The graphical representation of the solution is shown below.

Unfortunately, the integral has no analytical representation. However, we can find an analytical representation of $P_{eff}(t)$ by replacing the exponential and the square root within the integral by their Taylor expansion up to the third term in the Maple V © program (in annex) and up to the second term in the Mathematica 3.0© program (in annex), in the appropriate regions. For further detailed work on the analytical solution, see the Maple V © annex. The expansion must be limited to avoid the use of unconvenient exponential integrals in the analytical result.

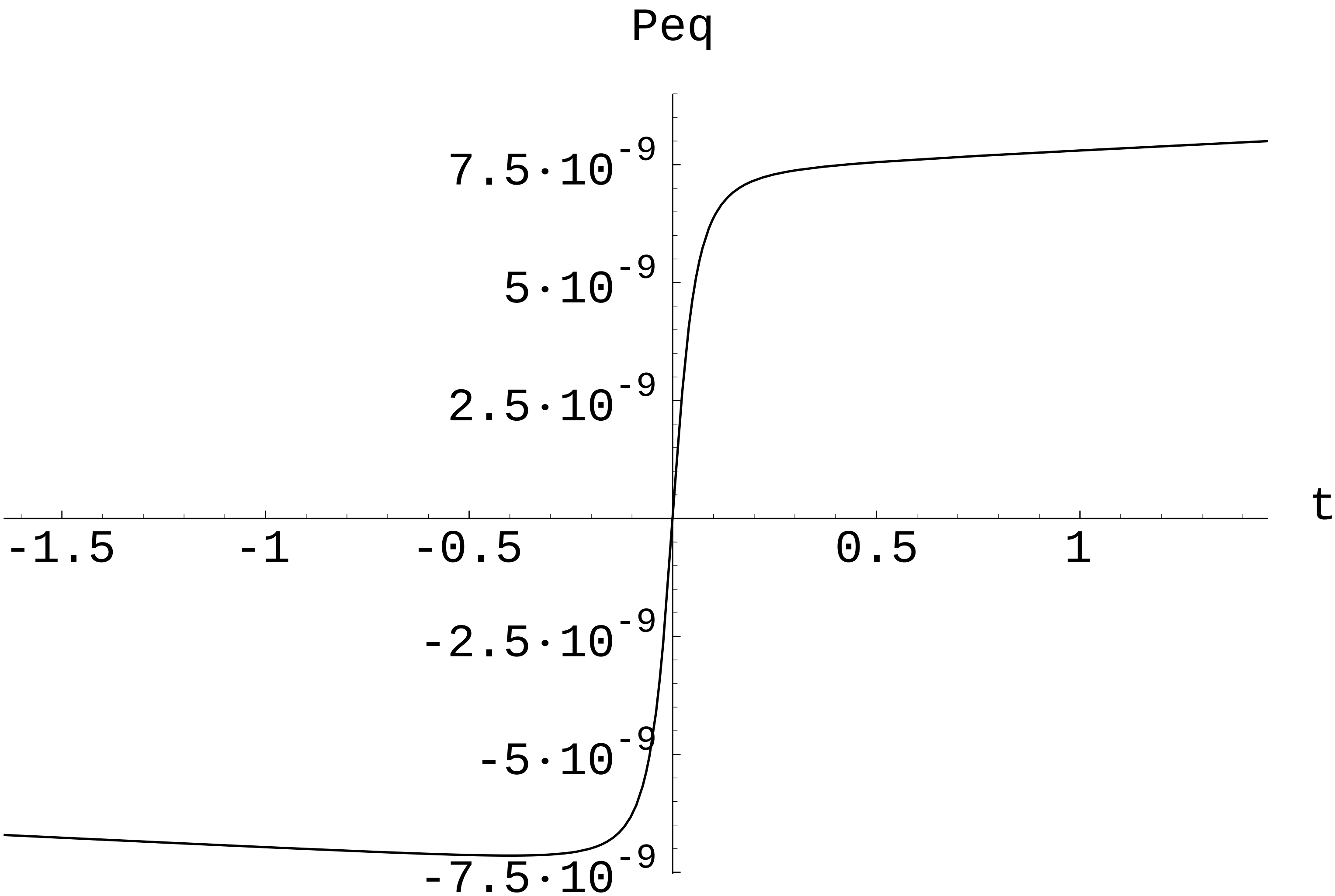

Figure 5: Evolution of P_{eq} as a function of time.

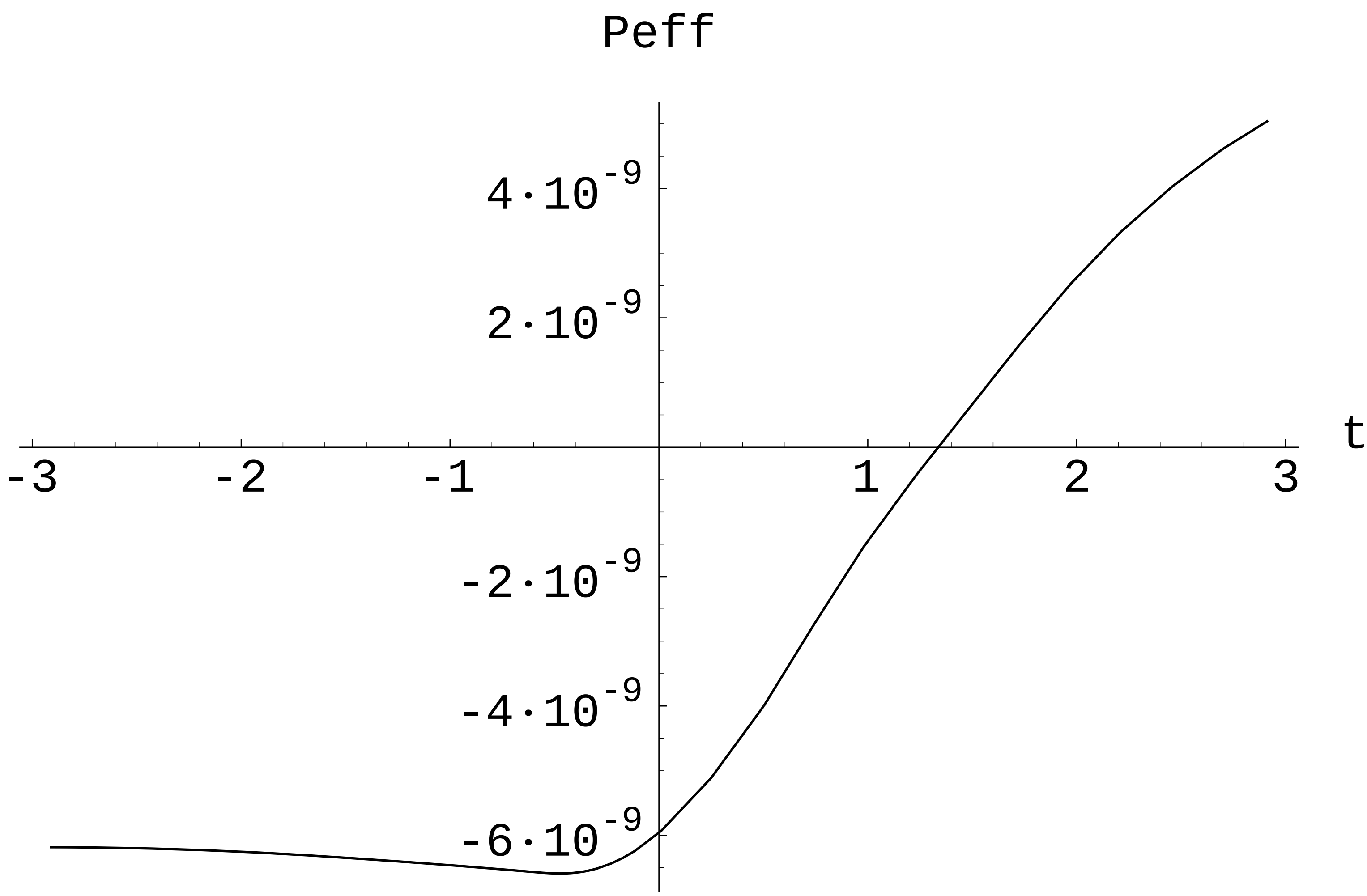

Figure 6: Evolution of P_{eff} as a function of time. When the sweep starts, $\vec{P_{eff}}$ is anti-aligned with the effective holding field which is pointing mainly toward the negative values of z. After the sweep, they are both pointing in the same direction, toward the positive values of z. P_{eff} goes to zero after the resonance.

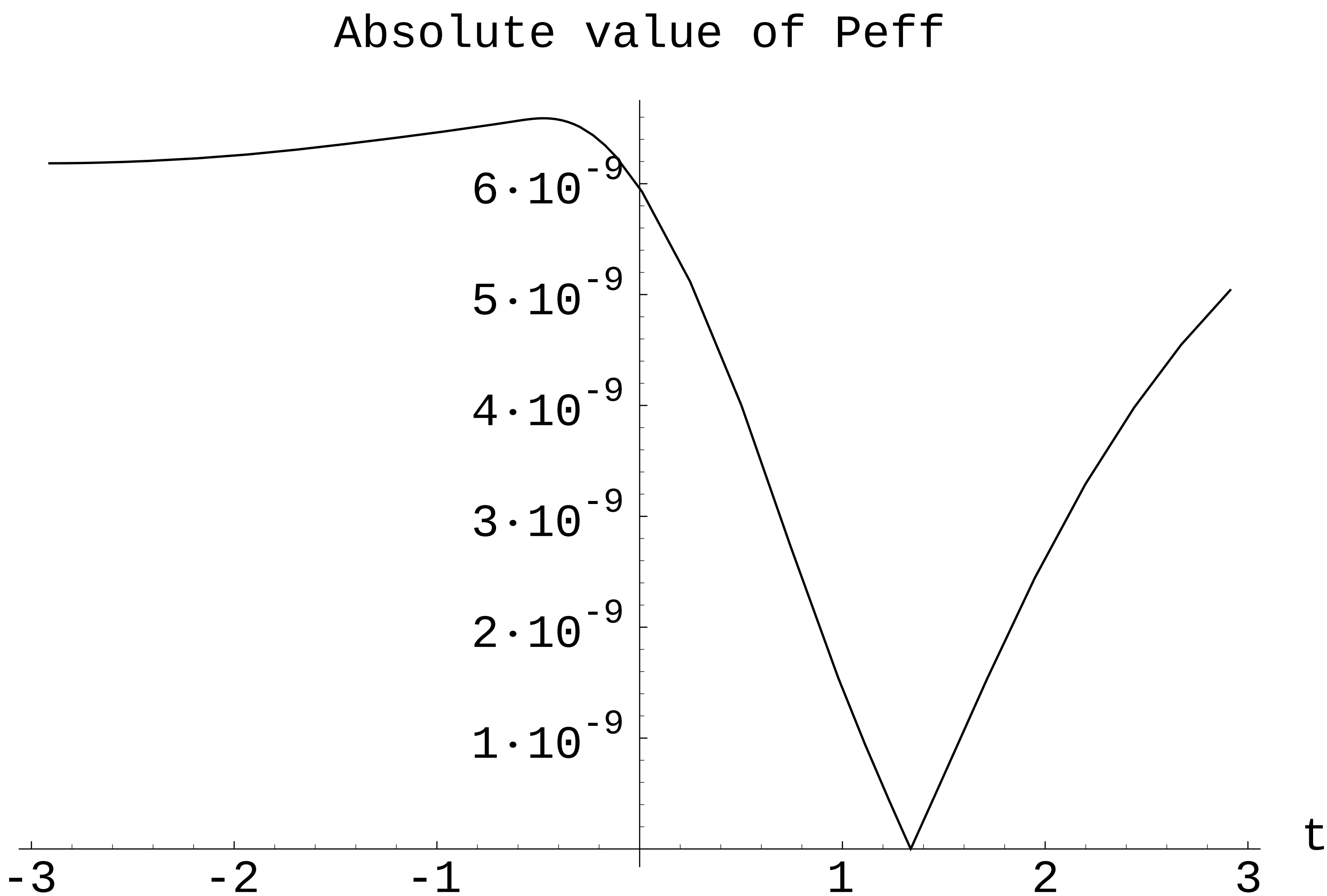

Figure 7: Evolution of the absolute value of P_{eff} as a function of time. This graph is expected to be the same as the modulus of P, obtained by numerical integration of the three Bloch equations.

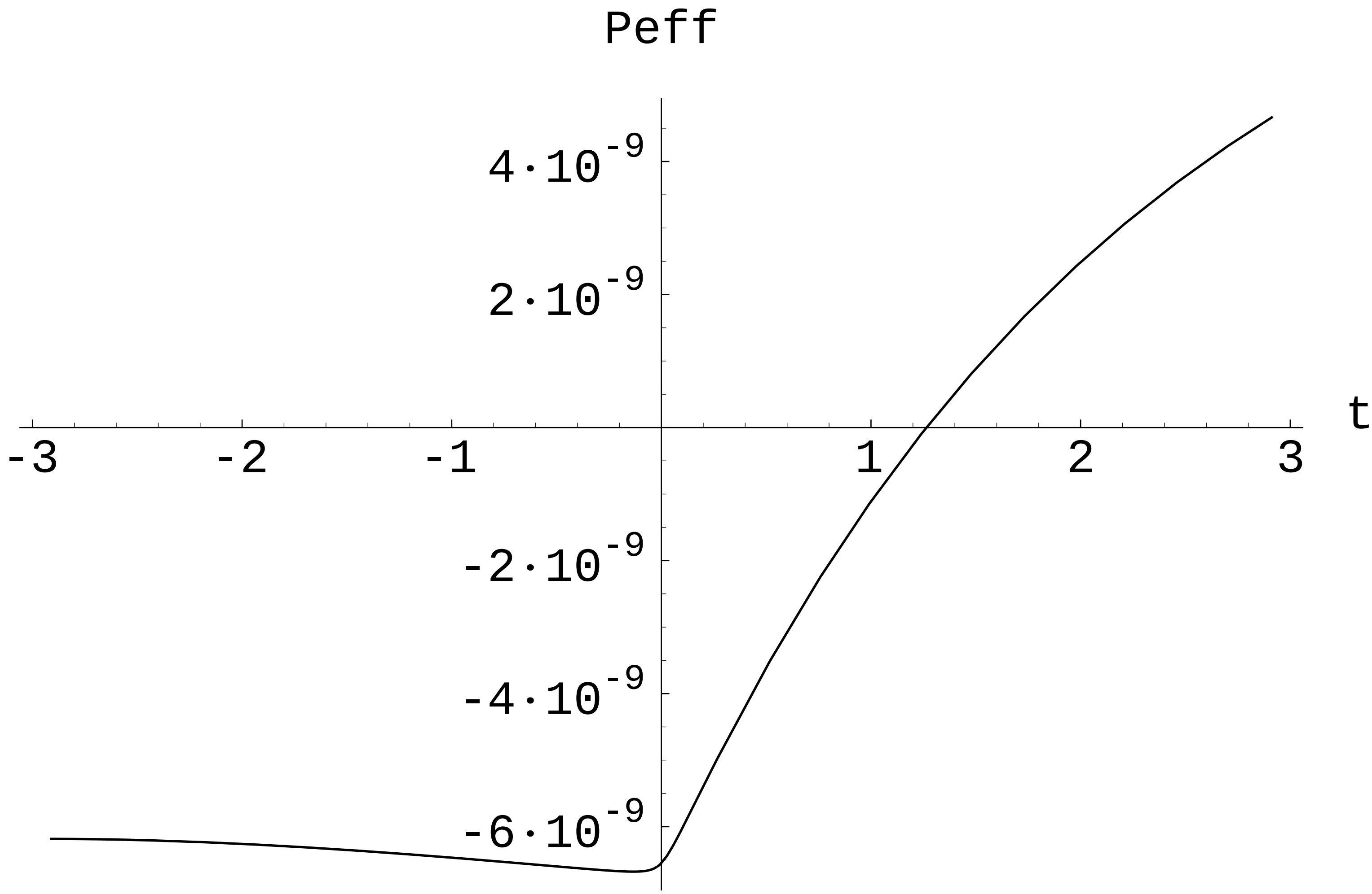

Figure 8: Evolution of P_{eff} as a function of time, obtained by plotting the solution of the differential equation.

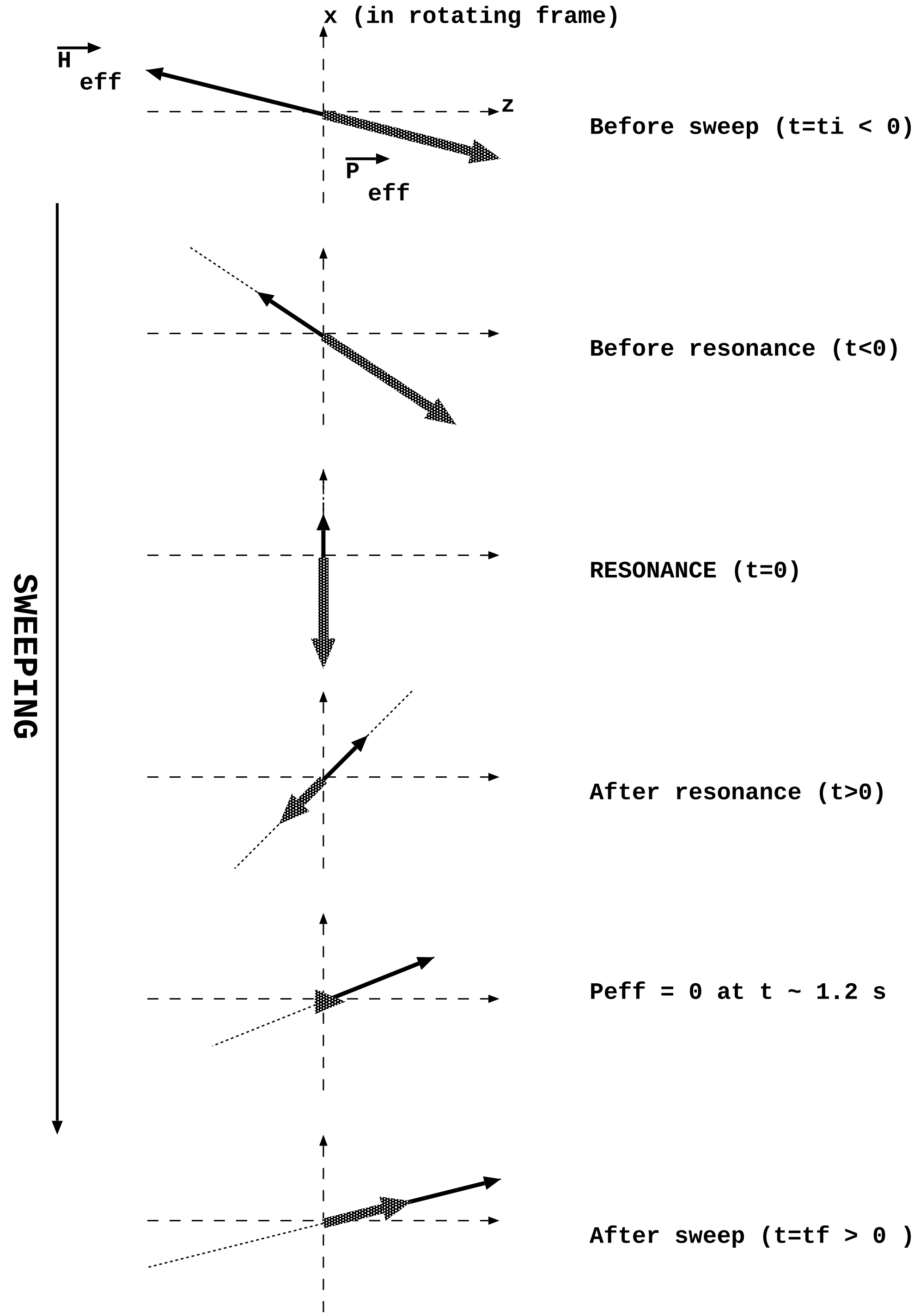

Figure 9: Animation representing the evolution of $\vec{H_{eff}} = H_1\hat{x} + (H - H_0)\hat{z}$ and $\vec{P_{eff}}$ as a function of time, in the rotating frame, in rotation around the $\hat{z}$ axis at the angular frequency $f = 91$ kHz. The picture is not drawn in scale.

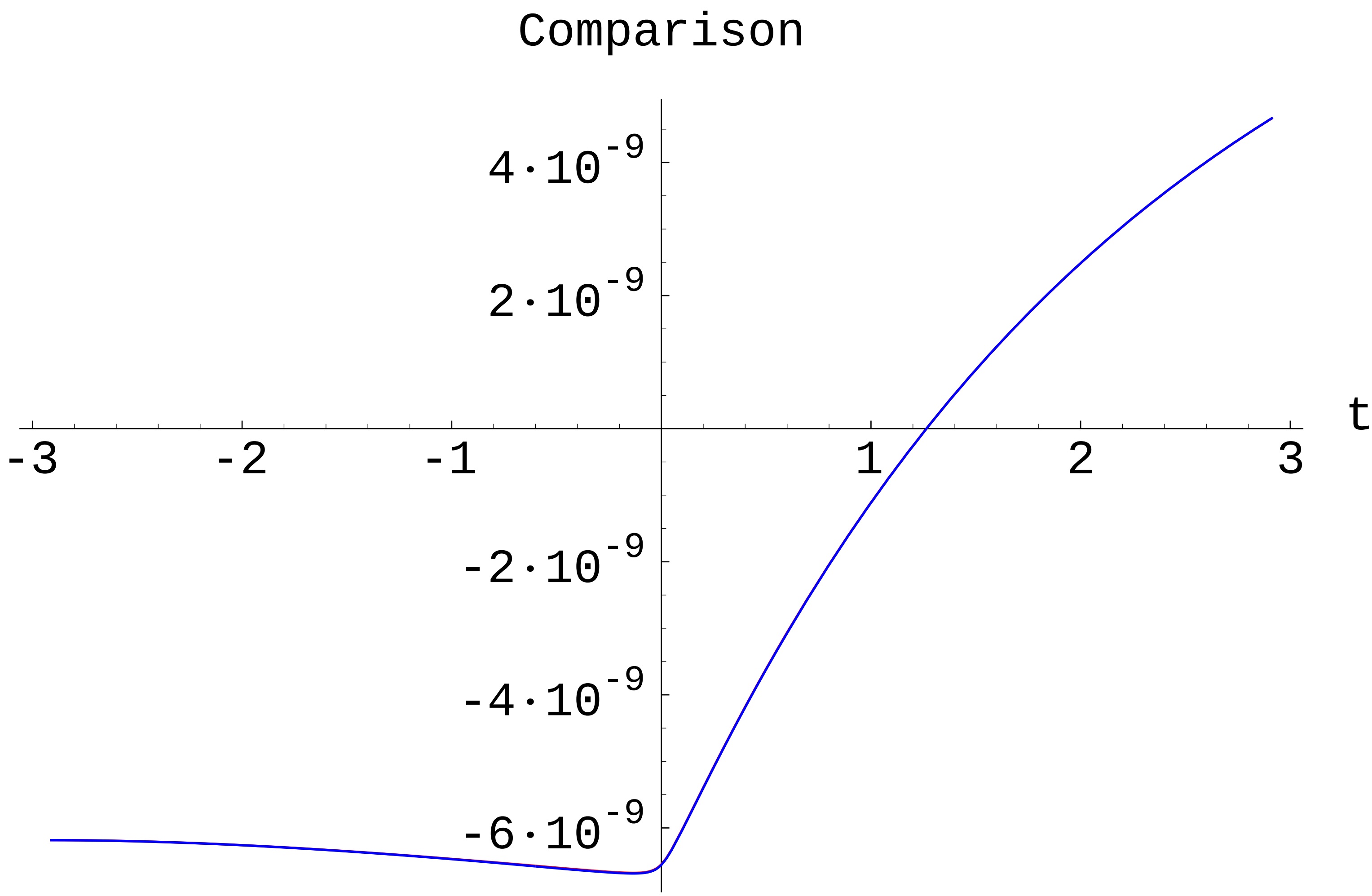

Figure 10: Plot as a function of time of the analytical solution and of the numerical solution of the differential equation satisfied by P_{eff}.

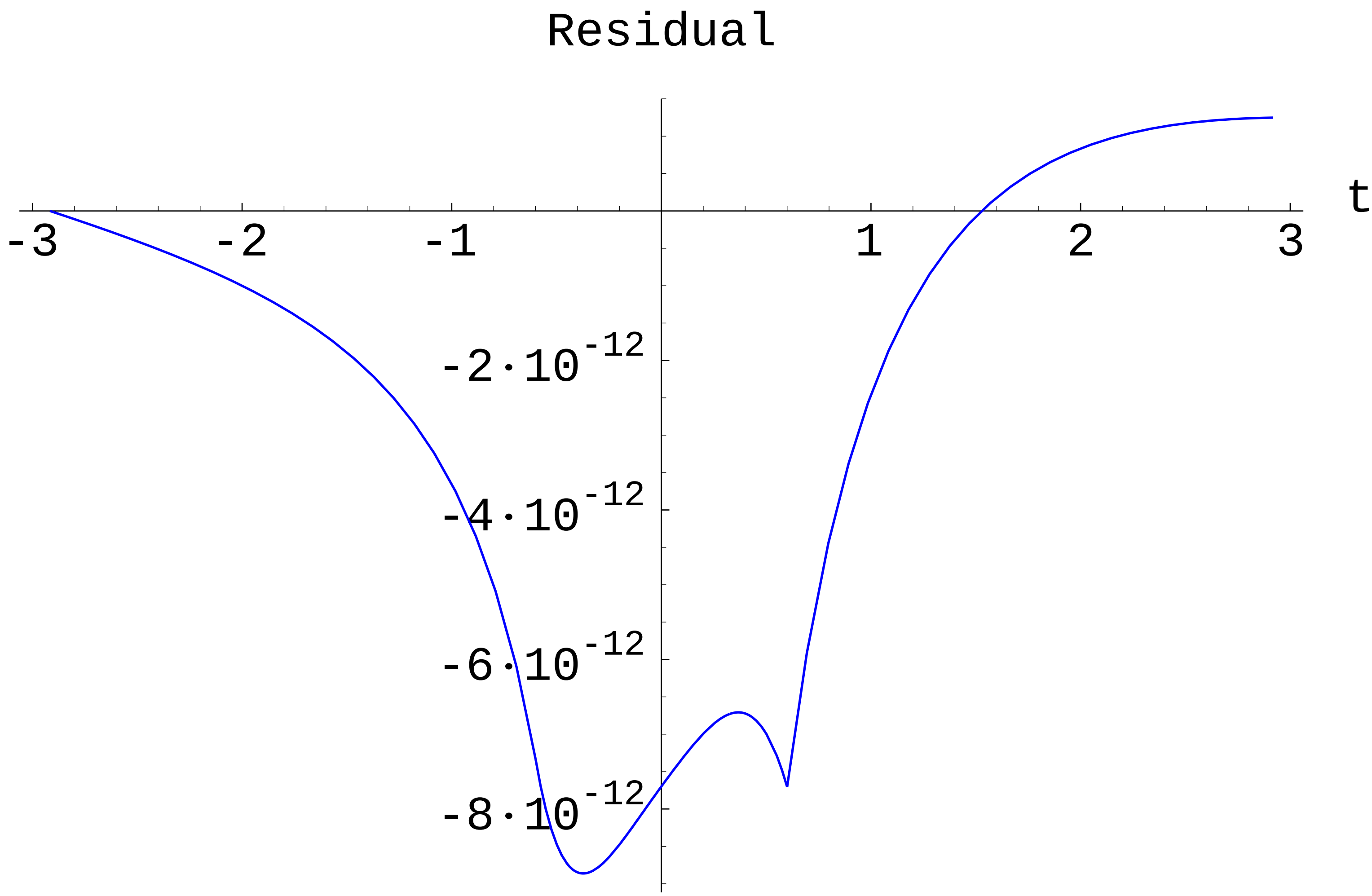

Figure 11: Difference as a function of time between the analytical solution and the numerical solution of the differential equations satisfied by P_{eff}. The values of t_a and t_b are chosen to minimize the residual at the resonance (at $t = 0$).

- if $t_i \leq t < t_a$, $\alpha|t| >> H_1$ then we can approximate the square root contained in the expression of $P_{eq}(t)$:

$$\frac{H_1^2 + H_0\alpha u + \alpha^2 u^2}{\sqrt{H_1^2 + \alpha^2 u^2}} \simeq -\frac{H_0\alpha u + \alpha^2 u^2}{\alpha u}\frac{1}{\sqrt{1 + \frac{H_1^2}{\alpha^2 u^2}}} \simeq -(H_0 + \alpha u) \tag{20}$$

The solution in that region is :

$$P_{eff}(t) \simeq e^{-(t-t_i)/T_1}\left[P_{eq}(t_i) - \frac{\chi}{T_1}\int_{t_i}^{t} e^{(u-t_i)/T_1}(H_0 + \alpha u)du\right] \tag{21}$$

- if $t_a \leq t < t_b$, $|u| << T_1$ then we can expand the exponential contained in the integral :

$$e^{(u-t_i)/T_1} \simeq e^{(-t_i/T_1)}\left(1 + \frac{u}{T_1} + \frac{u^2}{2T_1^2}\right) \tag{22}$$

The solution in that region is then :

$$\begin{aligned} P_{eff}(t) \simeq e^{-(t-t_i)/T_1}[P_{eq}(t_i) & - \frac{\chi}{T_1}\int_{t_i}^{t_a} e^{(u-t_i)/T_1}(H_0 + \alpha u)du \\ & + \frac{\chi}{T_1}e^{-t_i/T_1}\int_{t_a}^{t}(1 + \frac{u}{T_1} + \frac{u^2}{2T_1^2})\frac{H_1^2 + H_0\alpha u + \alpha^2 u^2}{\sqrt{H_1^2 + \alpha^2 u^2}}du] \end{aligned} \tag{23}$$

- if $t_b \leq t < t_f$, $\alpha|t| >> H_1$ we approximate the square root contained in the expression of $P_{eq}(t)$:

$$\frac{H_1^2 + H_0\alpha u + \alpha^2 u^2}{\sqrt{H_1^2 + \alpha^2 u^2}} \simeq \frac{H_0\alpha u + \alpha^2 u^2}{\alpha u}\frac{1}{\sqrt{1 + \frac{H_1^2}{\alpha^2 u^2}}} \simeq H_0 + \alpha u \tag{24}$$

The solution in that region is :

$$\begin{aligned} P_{eff}(t) \simeq e^{-(t-t_i)/T_1}[P_{eq}(t_i) & - \frac{\chi}{T_1}\int_{t_i}^{t_a} e^{(u-t_i)/T_1}(H_0 + \alpha u)du \\ & + \frac{\chi}{T_1}e^{-t_i/T_1}\int_{t_a}^{t_b}(1 + \frac{u}{T_1} + \frac{u^2}{2T_1^2})\frac{H_1^2 + H_0\alpha u + \alpha^2 u^2}{\sqrt{H_1^2 + \alpha^2 u^2}}du \\ & + \frac{\chi}{T_1}\int_{t_b}^{t} e^{(u-t_i)/T_1}(H_0 + \alpha u)du] \end{aligned} \tag{25}$$

4 Analytical Function to Fit the Water Data

We give below the analytical expression of the function $f(H)$ that should be used to fit the water data, assuming $T_1 = T_2$:

$$f(H) = a\frac{g(H - H_{res})}{g(0)}\frac{H_1}{\sqrt{[H - H_{res}]^2 + H_1^2}} + b[H - H_{res}] + c \tag{26}$$

with :

- if $t_i \leq t < t_a$, that is $H_{min} \leq H < H_a$:
  $g(x) = F_1(x)$
- if $t_a \leq t < t_b$, that is $H_a \leq H < H_b$ and $H_a \leq H_{res} < H_b$:
  $g(x) = F_2(x)$ and $g(0) = F_2(0)$
- if $t_b \leq t < t_f$, that is $H_b \leq H < H_{max}$:
  $g(x) = F_3(x)$

where

- $H_a = (H_{res} + \alpha t_a)$
- $H_b = (H_{res} + \alpha t_b)$
- the functions F_1, F_2 and F_3 are given in a Fortran form in the Mathematica 3.0© output.

H is simply the field value on the $\hat{z}$ axis saved in the NMR data files. The five unknown parameters to be found by the fitting program are : a, b, c, H_{res}, and H_1.

The optimal values of t_a and t_b have been calculated to minimize the difference between the numerical integration of the differential equations satisfied by P_{eff} and the Taylor expansions of the solution. We suggest :

$$t_a = -t_b = -0.6s \tag{27}$$

estimated for $T_1 = T_2 = 2$ s and using the numerical parameters introduced in the first section (γ, f, H_0, α, μ_{p,H_2O}, k, the temperature T and H_1). Therefore,

- $H_a = (H_{res} + \alpha t_a)$
- $H_b = (H_{res} - \alpha t_a)$

A water signal fit is shown below on Figure 12.

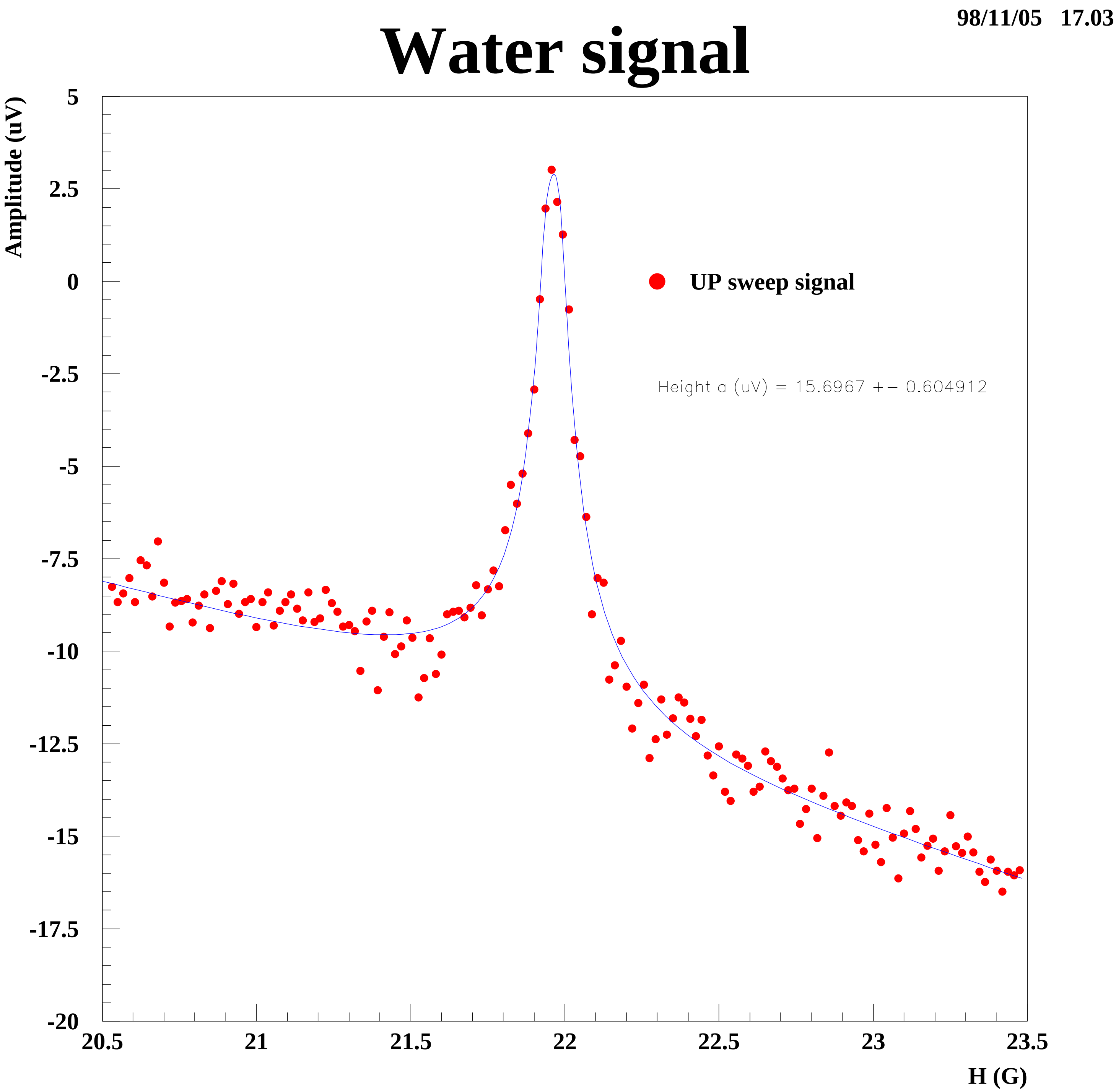

Figure 12: Fit of a sample of averaged water data using the analytical expression of the shape presented in this document, for a sweep from $H = 18$ G to $H = 25$ G. The fit has been performed with PAW© and gives a reduced χ^2 of $\chi^2/f = 0.39$.

5 Acknowledgements

We would like to express our gratitude to Michael Romalis for his valuable help on the extraction of the water signal shape.

References

[1] A. Abragam, "The principles of nuclear magnetism", p. 54, Oxford University Press (1961)