PULSEE: A software for the quantum simulation of an extensive set of nuclear magnetic and quadrupole resonance observables

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Abstract

We present an open-source software for the simulation of observables in nuclear magnetic/quadrupole resonance experiments (NMR/NQR) on solid-state samples, developed to assist experimental research in the design of new strategies for the investigation of quantum materials inspired by the early NMR/NQR quantum computation protocols. The software is based on a quantum mechanical description of nuclear spin dynamics in NMR/NQR experiments and has been widely tested on both theoretical and experimental available results. Moreover, the structure of the software allows an easy generalization of basic experiments to more sophisticated ones, as it includes all the libraries required for the numerical simulation of generic spin systems. In order to make the program easily accessible to a large user base, we developed a user-friendly graphical interface and fully-detailed documentation. Lastly, we portray several examples of the execution of the code that demonstrate the potential of NMR/NQR for the scopes of quantum control and quantum information processing.

Keywords: Nuclear magnetic resonance; Nuclear quadrupole resonance; Quadrupolar interaction; Nuclear spin dynamics; NMR/NQR quantum computing; Python 3
Program Title: PULSEE (Program for the simUlation of nuclear Spin Ensemble Evolution)

CPC Library link to program files: (to be added by Technical Editor)
Developer’s repository link: https://github.com/DavideCandoli/PULSEE
Code Ocean capsule: (to be added by Technical Editor)
Licensing provisions: GPLv3
Programming language: Python 3

Nature of problem: Applications of nuclear magnetic/quadrupole resonance techniques to study the properties of materials often requires extensive spectral simulations. On the other hand, applications of magnetic resonance techniques to quantum information science (QIS) involves different set of observables. Available simulation software address only one of these applications, that is, either detailed spectral simulations [1] and/or QIS relevant observables [2]. Therefore, there is a need for an up-to-date and easily accessible software for the simulation of an extensive set of nuclear magnetic/quadrupole resonance experimental observables that allow to reproduce the behaviour/response of nuclear systems with varying degree of complexity.

Solution method: The open-source Python code provides an extensive set of libraries for the simulation of the time evolution of nuclear spins in the presence of specific interactions and the reproduction of spectra and other observables measured in nuclear magnetic/quadrupole resonance experiments. The ready-to-use software features a user-friendly graphical interface.

References

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1. Introduction

Nuclear magnetic and quadrupole resonance (NMR/NQR) have a long-standing reputation as accurate methods for the microscopic investigation
of materials based on remarkably simple working principles. In addition to being a dominant tool in chemistry, materials science, structural biology and medicine, NMR represents an essential tool in QIS [1]. NMR also allows for fundamental tests of quantum mechanics [2] and fundamental condensed matter physics, as well as for probing microscopic spin and charge properties of materials [3–6]. These features are the reason for the success of magnetic resonance techniques in implementing one of the first quantum information processors: the high degree of control of nuclear spins that they provide lends naturally to the purposes of basic quantum computing, and has made it possible to witness for the first time the experimental realization of several quantum algorithms [7–15]. Specifically, the handling of quantum systems to perform data processing tasks in NMR is accomplished through the application of specific radio frequency (RF) pulses (logic gates) on ensemble states adequately prepared, called pseudopure states (PPS) [13, 14, 16–18]. The logic gates can be executed with high fidelity due to the high level of control of the quantum evolution of nuclear spins. The true power of a quantum computing lays in its ability to coherently manipulate entangled qubits. A 12-qubit NMR based quantum computer holds the record for the largest quantum computer, i.e. high fidelity implementation of a quantum algorithm with coherent manipulation of 12 qubits [19].

Nonetheless, the long term interest in the applications of NMR and NQR in quantum computing has faded since they present some major limitations when it comes to implementing a large scale quantum computer. However, the protocols developed for the manipulation of NMR/NQR qubits promise to be valuable resources for the exploration of unknown properties of materials. These methods may be used to highlight various features of NMR/NQR spectra, and in this way reveal important details of the underlying nuclear interactions.

Realizing protocols that enhance the power of NMR and NQR through the careful manipulation of nuclear spin degrees of freedom requires the development of a software that simulates such experimental techniques that feature the representation of nuclear spin states. To our knowledge, already existing programs that simulate NMR/NQR experiments are coded with outdated programming languages [20, 21], are based on closed-source software systems [22] or lack the density matrix visualization of spin states [23]: therefore, our purpose was to write an up-to-date software which could integrate all the features relevant for the current needs of research, making them fully accessible and extensively documented.
Our software PULSEE (Program for the simULation of nuclear Spin Ensemble Evolution) [24] is grounded on the quantum mechanical description of NMR and NQR, and is able to simulate the time evolution of nuclear spins in solid-state samples in a wide variety of configurations observed experimentally. After simulating the acquisition of the characteristic observable measured in NMR/NQR laboratories, such as for example the free induction decay signal (FID), one generates the NMR/NQR spectrum in a form which can be put in direct comparison with results coming from real experiments.

In section 2 we give an overview of the theory of NMR and NQR, including both the description of nuclear spin dynamics and the generation of the spectra from the analysis of the FID. In section 3 we present the simulation software, providing practical information about its installation, structure and usage. In section 4 we report several examples of simulations carried out with our software, which have been chosen due to their relevance for the purposes of quantum control and quantum information processing.

2. Theoretical background

Nuclear magnetic and quadrupole resonance (NMR/NQR) involve the time evolution of resonantly perturbed nuclear spins in matter. Experimentally, the distinction between the two methods lies in the different nuclear interactions being probed: NMR pertains to nuclei coupled to a local magnetic field (that is, an externally applied magnetic field), while NQR deals with the quadrupolar interaction between each nucleus and the surrounding electronic charges. From a theoretical point of view, though, it is convenient to treat the problem where both interactions are simultaneously present, since it includes all the possible intermediate configurations between pure NMR and pure NQR [5].

Our work focuses on the NMR study of single crystals, where assuming in first approximation that the nuclei are identical and non-interacting, each of them will be described by the same stationary Hamiltonian at thermal equilibrium:

\[ H_0 = H_Z + H_Q. \]  

Here, \( H_Z \) and \( H_Q \) stand for the Zeeman and quadrupolar interaction terms, respectively. The former represents the direct coupling between the nuclear intrinsic magnetic moment \( \gamma \hbar \mathbf{I} \) and the magnetic field \( \mathbf{B}_0 \) externally applied in the laboratory:

\[ H_Z = -\gamma \hbar \mathbf{I} \cdot \mathbf{B}_0, \]
where $\gamma$ is the gyromagnetic ratio of the spin, while $\hbar I$ is the spin operator of the nucleus. The term $\mathcal{H}_Q$, on the other hand, represents the interaction between the electric quadrupole moment of the nucleus and the electric field gradient (EFG) generated by the surrounding electrons, and in the coordinate system of the principal axes of the EFG it reads:

$$\mathcal{H}_Q = \frac{e^2 q Q}{4I(2I-1)} \left( 3I_Z^2 - I(I+1) + \frac{1}{2} \eta (I_+^2 + I_-^2) \right)$$

(3)

where $e$ is the elementary charge, $eq = V_{ZZ}$ is the largest eigenvalue of the EFG tensor, $eQ$ is the electric quadrupole moment, and $\eta$ is the asymmetry parameter of the EFG.

In NMR/NQR, one probes these interactions by sending a pulse of radiation onto the system, which accounts for a perturbing term to be included in the full Hamiltonian:

$$\mathcal{H}_1(t) = (2B_1 \cos(2\pi \nu_P t - \varphi_P)) \cdot I$$

(4)

where $2B_1$ is the magnetic component of the radiation pulse, $\nu_P$ and $\varphi_P$ its frequency and phase, respectively. This $B_1$ radiation field is in a plane perpendicular to externally applied magnetic field, $B_0$, that defines Zeeman quantization axis.

Before the application of any pulse, the system is found in its thermal equilibrium state, which at room temperature can be approximated as

$$\rho(0) = \frac{\exp(-\mathcal{H}_0/k_B T)}{Z} = (1 - \mathcal{H}_0/k_B T)/Z.$$  

Computing the evolution of this state under the action of a pulse is equivalent to finding the corresponding evolution operator $U(t_P, 0)$, where $t_P$ is the time duration of the pulse. In the most general case, this operator cannot be computed directly, since the full Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$ may depend on time. The procedure followed by our software consists of two steps:

i. The problem is cast to the interaction picture, where the only relevant term of the Hamiltonian is the perturbing one:

$$\mathcal{H}(t) \rightarrow \mathcal{H}_{\mathcal{H}_0}(t) = \exp(i\mathcal{H}_0 t/\hbar)\mathcal{H}_1(t) \exp(-i\mathcal{H}_0 t/\hbar).$$

(5)

ii. The evolution operator is approximated retaining the first few terms of the Magnus expansion [25, 26], computed through the following formulas:

$$\Omega_1(t_P, 0) = \int_0^{t_P} dt_1 \tilde{\mathcal{H}}(t_1)$$

(6)
\[
\Omega_2(t_P, 0) = \frac{1}{2} \int_0^{t_p} dt_1 \int_0^{t_1} dt_2 [\tilde{H}(t_1), \tilde{H}(t_2)]
\]  
from which the evolution operator is readily computed as

\[
U(t_P, 0) = \exp(\Omega_1(t_P, 0) + \Omega_2(t_P, 0) + \Omega_3(t_P, 0)).
\]

The software is also able to generate and analyze the typical observable measured in real NMR/NQR experiments, i.e. the free induction decay signal (FID). In laboratories, the FID is the electrical signal induced in a coil wound around the sample after the electromagnetic RF pulse which generates \(B_1\) field is switch-off. This signal is simply related to the component of the sample’s magnetization along the axis of the coil, related to the FID itself [27]. If the coil is oriented along \(\hat{n}\), then the FID signal will be given by:

\[
S(t) = \text{Tr} [\rho(t) \hat{n} \cdot I \exp(-t/T_2)] \quad t > t_P
\]

where we replaced the magnetization with the spin operator \(I\) of a single nucleus in the ensemble, since they are equal up to a scaling factor. Moreover, we introduced an empirical exponential decay \(\exp(-t/T_2)\) to account for the decoherence of spin ensemble. In effect, our software generates a complex FID whose imaginary part represents the signal produced by an additional coil orthogonal to \(\hat{n}\), so that in the most usual situation the FID reads \(S(t) = \text{Tr} [\rho(t) I_+ \exp(-t/T_2)]\).

Once the FID is acquired, one typically computes its Fourier transform to obtain what is called the NMR/NQR spectrum. This is the main outcome of the experiment and provides information about the interactions experienced by the system and the that of transitions occurred in its evolution. This is shown by the expansion of the FID in Fourier components:

\[
S(t) = \sum_{\varepsilon, \eta} \langle \varepsilon | I_+ | \eta \rangle \langle \eta | \rho(t_P) | \varepsilon \rangle \exp(i\omega_{\varepsilon, \eta} t)
\]

where \(\varepsilon, \eta\) run over the energy eigenvalues of the system, \(|\varepsilon\rangle, |\eta\rangle\) are the corresponding eigenstates, and \(\omega_{\varepsilon, \eta}\) is the frequency of transition between these two. This formula proves that the peaks of the NMR/NQR spectrum are located at the resonance frequencies \(\omega_{\varepsilon, \eta}\), and that some of these frequencies may not show up in the spectrum if the associated transition has not occurred or the detection setup is not oriented appropriately.
3. Structure and usage of the software

PULSEE is not simply a simulator of the time evolution of nuclear spin states, but also reproduces all the main features of NMR/NQR experiments. In this way, the program is a valuable tool in experimental research, as the outcomes of a simulation are generated in a form that can be directly compared with the results measured in laboratories.

3.1. Download, dependencies and launching

The software can be downloaded from the following GitHub repository: https://github.com/DavideCandoli/PULSEE

PULSEE has been written entirely in Python 3.7. The program makes wide use of many of the standard Python modules (namely numpy, scipy, pandas, matplotlib) for its general purposes. Tests have been carried out using the pytest framework and the hypothesis module. The software includes a GUI which has been implemented with the tools provided by the Python library kivy. In order to run the GUI, the installation of the additional modules kivy.garden and garden.matplotlib.backend_kivy is required.

The GUI is launched in the directory Code entering the following command from terminal

$ python PULSEE_GUI.py

Otherwise, one may use the functions defined in the module Simulation to write a custom simulation, as outlined in subsection 3.3.

3.2. Modules of the software

The program consists of 6 modules. Below, the content and role of each module is reported briefly:

1. Operators

This module, together with Many_Body, is to be considered a sort of toolkit for the simulation of generic quantum systems. It contains the definition of Python classes and functions related to the basic mathematical objects which enter the treatment of a quantum system. Operators concerns with the simulation of a single system, while Many_Body extends it to systems made up of several particles.
2. **Many_Body**
   It contains the definitions of the functions `tensor_product` and `partial_trace` which allow to pass from a single particle Hilbert space to a many particle space, and viceversa.

3. **Nuclear_Spin**
   Here is where the classes representing the spin of an atomic nucleus or a system of nuclei are defined.

4. **Hamiltonians**
   This file includes the definition of the relevant terms of the Hamiltonian of a nuclear spin system in a typical NMR/NQR experiment: namely, these are the Zeeman interaction, the quadrupolar interaction, the $J$-coupling between nuclei, and the interaction with an RF pulse of radiation.

5. **Simulation**
   This is the module the user should refer to in order to implement a custom simulation. The functions defined here allow to set up the nuclear system, evolve it under the action of a sequence of pulses, generate the FID signal, and compute the NMR spectrum from it.

6. **NMR_NQR_GUI**
   This is the graphical user interface of the program. The GUI provides a simple and intuitive way to perform a simulation, but it has limited features with respect to a custom simulation code: in order to reproduce complicated experiments involving long pulse sequences or many spin systems, one should make use of the latter.

3.3. **Building up a simulation**
   The starting point of any simulation is the set up of the system under study, which is done by calling the function `nuclear_system_setup`:

   ```python
   nuclear_system_setup(spin_par, quad_par=None, zeem_par=None, j_matrix=None, initial_state='canonical', temperature=1e-4)
   ```

   This function returns three objects representing the spin system, the unperturbed Hamiltonian, and the initial state, respectively.

   The next step is to evolve the state of the system under the action of a pulse of radiation, a task carried out by the function `evolve`:
The function not only allows to specify the features of the pulse applied to
the system, but also the reference frame where the evolution is computed.

Once the evolved state is obtained as the outcome of \texttt{evolve}, one can
generate the FID signal associated with this state by calling the function
\texttt{FID_signal}

\begin{verbatim}
FID_signal(spin, h_unperturbed, dm, acquisition_time, T2=100, \ntheta=0, phi=0, reference_frequency=0)
\end{verbatim}

The arguments of this function allow the user to set the time window of
acquisition of the FID, the decoherence time $T_2$, the orientation, and the
frequency of rotation of the detecting coils.

Eventually, one computes the NMR/NQR spectrum from the FID signal
by passing the FID through the function \texttt{fourier_transform_signal}

\begin{verbatim}
fourier_transform_signal(times, signal, frequency_start, \n    frequency_stop, opposite_frequency=False)
\end{verbatim}

The module \texttt{Simulation} includes also the functions for plotting the den-
sity matrix of the evolved state as well as the FID signal and NMR/NQR
spectrum.

4. Examples of execution

In this section we illustrate some noteworthy simulations performed with
PULSEE. In addition to being valid examples of the execution of the code,
these simulations have been chosen because they clearly demonstrate the
precision of NMR and NQR in the control of nuclear spin degrees of freedom,
which reflects their accuracy in the determination of unknown nuclear
interactions in a sample under study.
$\Delta m = \frac{1}{2}$

$-\frac{1}{2}$

$\frac{3}{2}$

$-\frac{3}{2}$

$\Delta m = 1$

$\Delta m = 2$

Figure 1: Scheme of the energy spectrum and the available transitions of a quadrupolar nucleus of spin 3/2. The transitions labeled with $|\Delta m| = 1$ involve the exchange of a single photon, while those labeled $|\Delta m| = 2$ involve two photons.

4.1. Selective transitions between quadrupolar states by means of properly polarized pulses in NQR experiments

The structure of the energy spectrum of quadrupolar nuclei allows for the selective excitation of its states by applying a pulse of radiation with the proper polarization.

A first notable example is represented by the pure NQR of a spin 3/2 nuclei whose energy levels and available transitions are depicted in Figure 1. This system may undergo two single photon transitions at the same frequency, namely $|1/2\rangle \leftrightarrow |3/2\rangle$ and $|-1/2\rangle \leftrightarrow |-3/2\rangle$, in contrast with a pure NMR experiment, where all the transitions are characterised by the same variation of the magnetic quantum number $\Delta m$. These two transitions imply an opposite change in the angular momentum of the system, so that each of them can occur only under exchange of a photon with circular polarization (c.p.) $\sigma^+$ and $\sigma^-$ respectively. Therefore, when one irradiates the system by a linearly polarized (l.p.) resonant pulse, both transitions will be induced; in contrast, by choosing the proper polarization of the pulse one is able to select only one of the two. The potential of circularly and in general elliptically polarized RF pulses in NQR has been widely explored [28–30].

These theoretical expectations are correctly reproduced by our software. We simulated the pure NQR of a spin 3/2 $^{35}\text{Cl}$ nuclei in a potassium chlorate crystal (KClO$_3$), whose gyromagnetic ratio is $\gamma/2\pi = 4.17$ MHz/T and the quadrupolar resonance frequency is $\nu_Q = 28.1$ MHz [31]. We prepared the system in the initial state depicted in Figure 2. Then we performed two distinct simulations evolving the system under the action of a $\pi$ pulse with
polarization $\sigma^+$ or $\sigma^-$ respectively (in a classical picture such pulses rotate the initial nuclear magnetization by 180° clockwise and anticlockwise respectively), and the results obtained are shown in Figure 3. We note that the $\pi$ pulse is defined as that whose amplitude $B_1$ and time duration $t_P$ satisfy the equation

$$\gamma \alpha B_1 t_P = \pi$$

where $\gamma$ is the gyromagnetic ratio of the nucleus and $\alpha = \sqrt{I(I+1) - m(m+1)}$ is a factor depending on the transition being induced.

The evolved density matrices clearly show that a pulse with circular polarization $\sigma^+$ ($\sigma^-$) couples only with the transition between states $|1/2\rangle \leftrightarrow |3/2\rangle$ ($|1/2\rangle \leftrightarrow |-3/2\rangle$) by acting selectively on the two relevant energy eigenstates to induce a full inversion of their respective populations, in such a way that the total angular momentum is conserved.

Another experiment where the pulse can be set up to selectively induce transitions is the NQR of a spin 1 nucleus in the presence of an asymmetric EFG [5]. Due to the non-vanishing asymmetry parameter, the energy eigenstates of this system are no longer the spin eigenstates, but they read:

$$|0\rangle \qquad |\xi_{\pm}\rangle = (|1\rangle \pm |-1\rangle) / \sqrt{2}$$

Figure 2: Real part of the density matrix representing the initial state of the spin 3/2 nucleus in the simulation of a pure NQR experiment. The system is prepared in a classical distribution where the states at the ground level are equally populated.
The energies of these states and the frequencies of transition between them are displayed in Figure 4. What is peculiar with this system is that in order for each of the three transitions to occur, the pulse should have a distinct linear polarization. Indeed, developing calculations one finds that

$$I_x = \begin{pmatrix} |\xi_+\rangle & |0\rangle & |\xi_-angle \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad I_y = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad I_z = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

from which it is easy to prove that an $\hat{x}$-, $\hat{y}$- or $\hat{z}$-polarized pulse will only affect the transition $|\xi_+\rangle \leftrightarrow |0\rangle$, $|\xi_-\rangle \leftrightarrow |0\rangle$ or $|\xi_+\rangle \leftrightarrow |\xi_-\rangle$, respectively. This behaviour can be assessed by observing the spectrum generated by each of these pulses: recalling equation (10), once the proper orientation of the detection coils is set, one is able to visualize if a certain transition has occurred, depending on the whether the term $\langle \eta | \rho(t_P) | \varepsilon \rangle$ vanishes or not.

These results have been simulated in a fictitious spin 1 nucleus with $e^2qQ/\hbar = 1$ MHz and asymmetry $\eta = 0.6$, for which the transition frequencies are $\nu_x \equiv \nu_{\xi_+\leftrightarrow 0} = 0.9$ MHz, $\nu_y \equiv \nu_{\xi_-\leftrightarrow 0} = 0.6$ MHz and $\nu_z \equiv \nu_{\xi_+\leftrightarrow \xi_-} = 0.3$ MHz. The resulting NQR spectra are displayed in Figure 5.
Figure 4: Scheme of the energy spectrum and the available transitions for a quadrupolar nucleus of spin 1 with an asymmetric EFG. The subscripts of the transition frequencies $\nu_x/y/z$ refer to the direction of linear polarization of the pulse required to induce each transition.

4.2. Generation of quantum coherences in a spin 3/2 quadrupolar nucleus

Let us consider the spin 3/2 $^{35}\text{Cl}$ nucleus in the same KClO$_3$ crystal introduced above. In the previous example, we showed how to induce a full inversion of the populations of two of its energy eigenstates, say $|m = 1/2\rangle$ and $|m + 1 = 3/2\rangle$, by means of a $\sigma^+$ c.p. $\pi$ pulse of radiation. In general, when the angle on the right-hand side of Equ. (11) is set to a value different from $n\pi$, where $n$ is an integer, the final density matrix exhibits non-zero off-diagonal elements, meaning that the evolved state includes a quantum superposition of $|m\rangle$ and $|m + 1\rangle$. In NMR, such elements are typically called “single quantum coherences”, where “single” specifies the fact that $\Delta m = 1$.

In Figure 6 we display the results of three simulated experiments where a pulse resonant with the $|1/2\rangle \leftrightarrow |3/2\rangle$ transition is applied and the angle in Equ. (11) is set to the values $\pi/3$, $\pi/2$ and $2\pi/3$, respectively. These simulations demonstrate it is possible to fine-tune the amplitudes of two states linked by a single-photon transition through the careful manipulation of the parameters of the pulse.

4.3. Preparation of an ensemble of spin 3/2 nuclei in a pseudopure state by means of NQR

NMR and NQR are naturally suited to the implementation of simple quantum information processors, as they are an efficient and high-precision...
Figure 5: Spectra resulting from three distinct simulations of the NQR of a spin 1 nucleus in an asymmetric EFG, where different pulses have been applied with polarization along \( \hat{x} \) (a), \( \hat{y} \) (b) and \( \hat{z} \) (c), respectively.
Figure 6: Results of the simulation of the NQR of $^{35}$Cl nuclei in a KClO$_3$ crystal where a pulse resonant with the $|1/2\rangle \leftrightarrow |3/2\rangle$ transition is applied. The three histograms show the real part of the density matrix of the system evolved after a: (a) $\pi/3$ pulse; (b) $\pi/2$ pulse; (c) $2\pi/3$ pulse. As the angle of rotation approaches $\pi$, the populations of the states involved in the transition undergo a continuous exchange, and at the same time non-zero off-diagonal elements emerge between them, meaning that the two states are in a quantum superposition.

method for manipulation of nuclear spins [32–36]. Nonetheless, in typical NMR/NQR experiments the system under study is a macroscopic sample made up of a huge number of nuclei, which makes it impossible to prepare it in a pure state as would be required by an ordinary quantum computation protocol. This problem has been addressed following a different strategy [7]: by means of a properly designed pulse sequence, the ensemble of nuclear spins can be prepared in a pseudopure state, i.e. a state $\rho = a\mathbb{1} + b|\psi\rangle\langle\psi|$ which differs from a pure state by a term proportional to the identity. A state of this kind is called pseudopure because, under evolution, it behaves like a full-fledged pure state. This property makes it the ideal starting point for any NMR/NQR quantum computation protocol [37–39].

In what follows, we describe a simulation of the NQR protocol aimed at realizing a 2-qubit pseudopure state in the ensemble of spin 3/2 quadrupolar $^{35}$Cl nuclei of a KClO$_3$ crystal [22], whose energy levels and available transitions have been already shown in Figure 1. The states of the 2-qubit computational basis correspond to the spin ones as follows:

\begin{align}
|00\rangle &\equiv |3/2\rangle \\
|01\rangle &\equiv |1/2\rangle \\
|10\rangle &\equiv |−1/2\rangle \\
|11\rangle &\equiv |−3/2\rangle .
\end{align}
Here, we remark that the simulated protocol is not aimed at implementing the pseudopure state in the physical system itself: such a state is obtained as the average of the results of three distinct experiments (as depicted in Figure 7), following a common practice employed in NMR/NQR called temporal averaging [40]. In each of the three experiments, the system is handled in a distinct way:

1. In the first, the system is left in its original thermal equilibrium state.
2. In the second, the system is irradiated by a c.p. pulse with resonant frequency $\nu_Q = (E_{z3/2} - E_{z1/2})/\hbar$, inducing one of the single photon transitions ($|\Delta m = 1|\rangle$). The time duration of the pulse is set to a value such that the populations of the states linked by the transition are exchanged.
3. In the third, a c.p. pulse at half the resonance frequency is applied, yielding one of the two-photon transitions ($|\Delta m = 2|\rangle$). Again, the time duration of the pulse accounts for the exchange of the populations of the states linked by the transition.

If the polarization of the pulses applied in the steps 2. and 3. are appropriately chosen the average of the density matrices resulting from the three
experiments will have the properties of a pseudopure state belonging to the computational basis in Equ. (14). The outcomes of the simulation, illustrating the real part of the density matrices representing the four pseudopure states of the computational basis of 2 qubits, are shown in Figure 8.

4.4. NQR and NMR implementation of a CNOT gate on a couple of qubits

Implementing a CNOT gate in the system we have already discussed in subsection 4.3 is a straightforward task. That is, in a 2-qubit system with \([0]\) and \([1]\) as only allowed input values for both qubits, the CNOT gate flips the second (target) qubit from \([0]\) to \([1]\) if and only if the first (control) qubit is in \([1]\) initial state. Indeed, one can easily check that the action performed by a CNOT\(_1\) gate on the 2-qubit system is equivalent to that of a pulse which yields an exchange of the populations of the states \([-1/2]\) and \([-3/2]\), as illustrated in Figure 9. The effect of this gate as simulated by our software is depicted in Figure 10.
Figure 9: Symbolic notation of a CNOT gate operating on the state $|10\rangle$ (on top) and the action of the pulse which carries out the equivalent operation on the NQR version of the 2-qubit system (at the bottom).

Figure 10: Input (on the left) and output (on the right) states of the simulated NQR CNOT$_1$ gate when the initial state is $|10\rangle$. 
It is possible to implement an analogous operation by means of NMR as well, but in a different nuclear system. As explained in [35], this time the 2 qubits are encoded in 2 distinct spin 1/2 nuclei (following the convention $|0\rangle \equiv |1/2\rangle$, $|1\rangle \equiv |{-1}/2\rangle$), and in order for them to work as a control-target qubit couple they must interact with each other. Thus, we assume that they are linked by the typical $J$-coupling, whose contribution to the Hamiltonian is:

$$\mathcal{H}_J = \hbar J I_z^{(1)} I_z^{(2)}$$

(15)

where $J$ is the coupling constant and $I_z^{(i)}$ is the $z$ component of the spin of the $i$-th nucleus. The experimental protocol for the implementation of an NMR CNOT gate employs both selective rotations of each spin as well as the free evolution of the whole system under the action of $J$-coupling, according to the sequence:

$$\text{CNOT}_1 = \left(-\frac{\pi}{2}\right)_z^I \left(\frac{\pi}{2}\right)_z^I \left(-\frac{\pi}{2}\right)_x^I U\left(\frac{1}{2J}\right) \left(-\frac{\pi}{2}\right)_y^I$$

(16)

Here, factors of the type $(\alpha)_{x/y/z}^I$ represent pulses resonant with the $i$-th spin which make it rotate an angle $\alpha$ around the axis specified in the subscript; $U\left(\frac{1}{2J}\right)$, on the other hand, stands for the free evolution of the system for a time duration of $1/2J$. We point out that in order to be able to perform selective rotations of one of the two spins, the nuclei’s gyromagnetic ratios must be appreciably different, leading to well separated gyromagnetic frequencies $\nu_0^{(i)} = -\left(\gamma^{(i)}/2\pi\right)B_0$.

We have carried out a simulation of this protocol starting from ideal pure input states. The outcomes match closely our expectations, i.e. initial ket is flipped since control (second) qubit was in $|1\rangle$ initial state, as is shown in Figure 11.

5. Conclusions

PULSEE is an open-source software for the simulation of nuclear magnetic/quadrupole resonance experiments (NMR/NQR) on solid-state samples. The main purpose of this program is to provide a numerical tool for the development of new methods of investigation of emergent properties in complex materials inspired by the NMR/NQR protocols established in the context of quantum information processing [41].
Figure 11: Input (on the left) and output (on the right) of the simulated NMR CNOT$_1$ gate when the initial state is set to the ideal pure state $|10\rangle$. The output state presents a slight discrepancy with respect to the expected $|11\rangle$ state, which is thought to be a consequence of the discrete approximations taken in the simulation.

The software follows the principles of wide accessibility and intuitive utilization, being available for download from a public GitHub repository [24] and providing a GUI, as well as a complete and detailed documentation.

The examples of execution we have discussed were meant to illustrate the features of the software, which include the ability to simulate both the evolution of spin states and the corresponding experimental observables and also highlight the possibilities to manipulate nuclear spin states through NM-R/NQR, which could be relevant for the design of highly sensitive protocols for the study of emergent quantum properties of materials.

6. CRediT author statement

Davide Candoli: Investigation, Software Programing, Development and Validation, Formal analysis, Visualization, Data curation, Writing-Original draft preparation. Samuele Sanna: Methodology, Investigation, Supervision, Formal analysis, Resources, Reviewing and Editing. Vesna F. Mitrović: Conceptualization, Methodology, Supervision, Formal analysis, Visualization, Resources, Writing-Reviewing and Editing.
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