Optimal control of molecular spin qudits

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We demonstrate, numerically, the possibility of manipulating the spin states of molecular nanomagnets with shaped microwave pulses designed with quantum optimal control theory techniques. The state-to-state or full gate transformations can be performed in this way in shorter times than using simple monochromatic resonant pulses. This enhancement in the operation rates can therefore mitigate the effect of decoherence. The optimization protocols and their potential for practical implementations are illustrated by simulations performed for a simple molecular cluster hosting a single Gd3+ ion. Its eight accessible levels (corresponding to a total spin $S = 7/2$) allow encoding an 8-level qudit or a system of three coupled qubits. All necessary gates required for universal operation can be obtained with optimal pulses using the intrinsic couplings present in this system. The application of optimal control techniques can facilitate the implementation of quantum technologies based on molecular spin qudits.

I. INTRODUCTION

A crucial challenge for the development of quantum simulation and quantum computation is to scale up computational power while keeping the processor robust against noise and limiting the complexity of control lines and electronics [1–3]. A promising strategy is to replace qubits with $d$-dimensional ($d > 2$) quantum systems, or qudits [4–6], as the elementary building blocks of the quantum architecture. The ability to integrate nontrivial operations in a single physical system helps simplifying some quantum algorithms [7–9]. In addition, it can also facilitate their implementation by reducing the number of nonlocal operations, i.e. those connecting different parts of the circuit.

Qubits have been realized with the multiple quantum states of diverse physical systems, including photons [10], trapped ions [11], impurity nuclear spins in semiconductors [12] and superconducting circuits [13]. Here, we focus on a special class of systems, molecular nanomagnets [14–18] (see Fig. 1 for an illustrative example). These are coordination or supramolecular complexes that consist of a magnetic core surrounded by a shell of organic ligand molecules. Chemistry offers nearly unbound possibilities for the design of spin qudits based on these molecules. The combination of one or several $S > 1/2$ transition metal or lanthanide ions with sufficiently weak magnetic anisotropy and/or exchange interactions gives rise to a number of low-lying magnetic levels. For suitably chosen molecular structures, these levels are unequally spaced, making transitions between them addressable via microwave resonant pulses. And nuclear spin states of the metal ions provide additional resources [19–23].

Examples of molecular based electronic and electronuclear spin qudits, with dimension $d$ ranging from 4 up to 64, have been reported recently [19–24]. In addition, there have been proposals for exploiting their multiple states to specific applications. Relevant examples are the digital quantum simulation of spin-boson models [31], where the qudit encodes boson states, and the implementation of quantum error correction codes [32–35]. The latter is particularly promising, as embedding in each basic unit, in this case a molecule, a suitably designed protection against its specific decoherence sources might represent a huge competitive advantage. Besides, the functionalities need not be defined a priori. When the allowed transitions between different qudit states form a universal set, these systems can be regarded as microscopic size universal processors (or NISQs) [18,22,27–29,33].

However, decoherence remains a serious limitation for fully unleashing the potential of these otherwise very appealing systems. Even though some specifically designed molecular spin qudits show remarkably long coherence times $T_2$ [35,36], decoherence tends to increase for higher spin or higher nuclearity molecules. A sequence of necessarily imperfect gates might become impractically long as compared to $T_2$, leading to large error rates. In the paradigmatic example of a qudit-based quantum error protocol, such effects can completely overcome the gain brought about by the code itself [30,32]. Clearly, this calls for more efficient methods to carry out such operations.

In this work, we consider the possibility of applying quantum optimal control theory (QOCT) techniques [38]...
to mitigate some of the limitations associated with the use of monochromatic resonant pulses. This theory allows designing more complex pulses in order to find the temporal shape of the external perturbation that makes the evolution operator equal to a predefined gate, as shown for the first time by Palao and Kosloff [39]. Numerous later calculations employing similar schemes have been reported [40–46]. We illustrate its application to the following expressions for $\hat{S}_z$ approximation [14, 47]. In this work, we have used the following expressions for $\hat{H}_{ZF}$ and $\hat{H}_{Zeeman}$

$$\hat{H}_{ZF} = D \left( S_z - \frac{1}{3} S(S + 1) \right) + E \left( \hat{S}_x^2 - \hat{S}_y^2 \right)$$

$$\hat{H}_{Zeeman} = -g\mu_B \vec{B} \cdot \hat{S}$$

where $S$ is the spin quantum number of the molecule, $(\hat{S}_x, \hat{S}_y, \hat{S}_z)$ are the spin operators, $D$ and $E$ are magnetic

![FIG. 1. Top: Schematic image of a molecular spin subject to a static magnetic field $\vec{B}$ and to an arbitrarily shaped microwave magnetic field $\vec{b}$, here generated by a transmission line. Bottom: spin energy levels of the GdW$_{30}$ polyoxometalate cluster [27, 37], whose structure is shown in the top. The 8 spin states, associated with the $S = 7/2$ spin of the central Gd$^{3+}$ ion, enable encoding a $d = 8$ qudit or three qubits. The coloured circular arrows mark the seven transitions that can be implemented by means of resonant monochromatic pulses.](image-url)
anisotropy constants, $g$ is the spin $g$-factor, and $\mu_B$ is the Bohr magneton. These expressions describe accurately the GdW$^{30}$ molecular spin qudit, which we use in section III below to illustrate the potential of QOCT techniques.

In particular, the uniaxial magnetic anisotropy $DS^2$ provides the level anharmonicity that is required to properly address individual transitions between the qudit states. Yet, the methodology is general and could be applied to more complex versions of the spin Hamiltonian adapted to diverse implementations (e.g. those including weakly coupled electronic spins or a combination of nuclear and electronic spin states).

The last term in Eq. (1) provides the ability to control the quantum spin states. As with the static terms, for the sake of simplicity we use the following form

$$\hat{H}_{\text{ctl}} = -g\mu_B f(t)\hat{b} \hat{S} \hat{\sigma}_z$$  \hspace{1cm} (4)

which corresponds to a time-dependent version of the Zeeman interaction term \(B\). This Hamiltonian describes the most common spin control techniques, based on electron paramagnetic resonance instrumentation, in which the absorption of this signal is the crucial observable. In recent times, it has been shown that spin qubits, including those in molecules, can also be manipulated by means of electric field pulses [48, 49]. In this case, the time-dependent perturbation introduces a modulation of the crystal field and the magnetic anisotropy terms associated with it. Again, the methods described below are easily adaptable to these situations.

### B. Coherent control via monochromatic resonant pulses

Often, the temporal shape is a simple monochromatic term, e.g.

$$f(t) = \lambda \cos(\omega t + \phi)\Pi_{t_0}^{t_f}(t),$$ \hspace{1cm} (5)

where the amplitude is determined by $\lambda$, and $\Pi_{t_0}^{t_f}(t)$ is the rectangular function, that is equal to one if $t_0 \leq t \leq t_f$, zero otherwise (in reality, of course, the ramp up and down at $t_0$ and $t_f$ are not abrupt). If the frequency is chosen to be close to one of the resonances, and the amplitude is low enough, the rotating wave approximation (RWA) may be applied, and the effect of these pulses can be worked out analytically: if $j, k$ are the two levels linked by the resonance (let us assume a perfect resonance, and that all other frequencies are well separated), the evolution operator $\hat{U}(t)$ is:

$$\hat{U}(t) = \hat{R}^{(jk)}_{\vec{n}}(\theta) \oplus \hat{1}^{(j\bar{k})}.$$  \hspace{1cm} (6)

This expression assumes the interaction representation, and, in order to simplify the notation, we have set $t_0 = 0$. The superindex $(jk)$ on the two-dimensional rotation operator $\hat{R}^{(jk)}_{\vec{n}}(\theta)$ means that it acts on the subspace spanned by the $j, k$ levels, whereas the rest of the levels are unaffected ($\hat{1}^{(j\bar{k})}$ is the identity in all but the $j, k$ levels). Within the basis spanned by the two states, $j, k$, and the corresponding Pauli matrices $\sigma_\alpha$ (in that basis), the rotation operator is given by:

$$\hat{R}^{(jk)}_{\vec{n}}(\theta) = \exp \left( -i \frac{\theta}{2} \vec{n} \cdot \mathbf{\sigma} \right).$$  \hspace{1cm} (7)

$\vec{n}$ is the coupling matrix. The rotation angle $\theta$ is $\lambda g \mu_B |\mu_{jk}| t$, where $\mu_{jk} = \langle j | \hat{b} \hat{S} \hat{\sigma}_z | k \rangle$ is the coupling matrix element, and $\vec{n}$ is the unit vector:

$$\vec{n} = (\cos(\arg \mu_{jk} + \phi), -\sin(\arg \mu_{jk} + \phi), 0).$$ \hspace{1cm} (8)

The choice of $\phi$ determines the rotation axis: if $\phi = -\arg \mu_{jk}$, we have a $R_X(\theta)$ rotation; if $\phi = -\arg \mu_{jk} - \pi/2$, we have a $R_Y(\theta)$ rotation. We cannot have direct $R_Z(\theta)$ rotations, but they can however be built by combinations of the former two. (we recall that here, $X, Y, Z$ do not refer to any spatial direction, but to the Pauli matrices defined in the basis spanned by the states $j, k$).

Let us consider $R_X(\theta)$ rotations in the following. By adjusting the total pulse time $t_f$, one selects the angle $\theta$ and, for example, performs a $\pi$-rotation, i.e. if:

$$t_f = t_f^\pi = \frac{\pi}{\lambda g \mu_B |\mu_{jk}|}$$ \hspace{1cm} (9)

the rotation transforms the $j$ state into the $k$ state and viceversa:

$$\hat{R}_X(\pi) = -i \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$ \hspace{1cm} (10)

Note the presence of the $-i$ factor; it is an irrelevant global phase factor if we consider the $(j, k)$ subspace as isolated, but it changes the phase with respect to the rest of the levels.

By concatenation of several of these rotations, one may attempt to construct arbitrary unitaries in any $2^n$-level system [18, 22, 27, 29]. Some specific quantum gates cannot be constructed in this way, however, due precisely to the presence of the phases mentioned above. This limitation can be remedied: see [9] for a discussion on this issue, and for an easy solution via the presence of an extra ancillary level.

The problem that cannot be remedied is the approximate character of all previous expressions, that rely on the weakness of the perturbation amplitude $\lambda$, thus avoiding the possibility of arbitrarily speeding up the process by increasing that amplitude. If we require a minimum fidelity for the $|j\rangle \rightarrow |k\rangle$ transformations, then a minimum amount of time is necessary.

### C. Quantum Optimal Control Theory (QOCT)

The previous arguments reveal an intrinsic limitation of monochromatic pulses for the creation of fast quantum gates, which may be further complicated by the
presence of experimental constraints, i.e. the inability
to increase the magnetic field intensities. In order to
create faster gates, one may attempt to use more com-
plex temporal shapes, i.e. combine various frequencies.
We therefore wonder how this possibility may help the
control of molecular spin qudits, i.e. whether operation
times can be made substantially shorter than the coer-
ce times. For this purpose, we have applied QOCT.
We summarize in the following the method and the basic
equations that we have employed.

We consider that the time-dependent pulse-shape func-
tion $f(t)$ alluded above is parameterized with a set of
values $u_0, \ldots, u_M \equiv w$: i.e. $f = f(u; t)$. The evolution
of the system is then determined by the Hamiltonian:

$$
\hat{H}(u; t) = \hat{H}_0 + f(u; t)\hat{V},
$$

(11)

where $\hat{H}_0 = \hat{H}_{ZF} + \hat{H}_{Zeeman}$, and $\hat{V} = -g\mu_B \hat{B}$.
The evolution operator $\hat{U}(u; t)$ is thus also determined
by $u$. In the interaction representation it evolves accord-
ing to:

$$
i\frac{\partial}{\partial t} \hat{U}(u; t) = f(u, t)\hat{V}(t)\hat{U}(u; t),
$$

(12)

$$
\hat{U}(u; 0) = \hat{I},
$$

(13)

where $\hat{V}(t) = \exp(i\hat{H}_0)\hat{V}\exp(-i\hat{H}_0)$.
The goal is to find a set of parameters $w^{(0)}$ such that
the evolution operator is equal – or equivalent – to a
given target gate $\hat{U}_G$: $\hat{U}(w^{(0)}, T) = e^{\hat{a}}\hat{U}_G$ for any irre-
levant global phase $a$. In the QOCT framework, this is
achieved by finding a set of parameters that leads to the
maximization of a functional of the system evolution; in
this case this can be done by defining this functional as:

$$
F(\hat{U}) = |\hat{U} \cdot \hat{U}_{\text{target}}|^2
$$

(14)

where the dot product in the space of linear transforma-
tions that we have used is the Fröbenius product:

$$
\hat{A} \cdot \hat{B} = \frac{1}{d} \text{Tr}[\hat{A}^\dagger \hat{B}].
$$

(15)

Here, $d$ is the space dimension. The functional thus
defined acquires its maximum value (one) when $\hat{U}$ is equal
to the target gate, modulo a phase factor. Since, as men-
tioned above, the evolution is determined by the param-
eters $u$, the problem is reduced to the maximization of the
function:

$$
G(u) = F \left[ \hat{U}(u; t_f) \right].
$$

(16)

Many possible algorithms exist for finding the maxima of
multivariate functions such as $G$. Most of them require
of a means to compute the gradient of the function (in
addition to the function itself). Optimal control theory
provides the mathematical tool to derive these gradients
(essentially, Pontryagin’s maximum principle [20]). For
the case of our function $G$, the gradient is given by:

$$
\frac{\partial G}{\partial u_m}(u) = 2\text{Im} \int_0^{t_f} dt \frac{\partial f}{\partial u_m}(u; t) \hat{B}(u; t) \cdot (\hat{V}(t)\hat{U}(u; t)),
$$

(17)

where the costate $\hat{B}$ is defined by the following equa-
tions:

$$
\frac{\partial}{\partial t} \hat{B}(u; t) = f(u, t)\hat{V}(t)\hat{U}(u; t),
$$

(18)

$$
\hat{B}(u; t_f) = (\hat{U}_{\text{target}} \cdot \hat{U}(t_f))\hat{U}_{\text{target}}.
$$

(19)

Note that it is an equation of motion similar to the one
that determines the evolution operator itself, except the
boundary condition is given at the final time of the prop-
agation $t_f$ (it is a final condition, instead of an initial
condition). In consequence, the computation of the gra-
dient requires two propagations: a forward propagation
for $\hat{U}$, and a backward propagation for $\hat{B}$.

It remains to specify the parameterization of $f$, an
important task that actually defines the set of allowed
temporal shapes. This should be done with the experi-
mental capabilities in mind. In our case, we have opted
for a simple Fourier expansion:

$$
f(u, t) = \frac{1}{\sqrt{t_f}} u_0 + \sum_{k=1}^K \left[ u_{2k} \frac{2}{\sqrt{t_f}} \cos(\omega_k t) + u_{2k-1} \frac{2}{\sqrt{t_f}} \sin(\omega_k t) \right].
$$

(20)

The frequencies $\omega_k = 2\pi k/t_f$, $k = 1, \ldots, K$ have a max-
imum cutoff value at $2\pi K/t_f$, that must be chosen big
enough to include the relevant natural frequencies of the
spin qudit, but not so large that it cannot be handled
experimentally.

Some constraints have to be imposed on the allowed
values for the parameters: the pulse amplitude must start
and end at zero: $f(u, 0) = f(u, t_f) = 0$, which translates
into $\sum_{k=1}^K u_{2k} = 0$. We have also imposed a zero value
for the average amplitude, $\int_0^{t_f} dt f(u, t) = 0$, which trans-
lates into $u_0 = 0$. Finally, the generated magnetic field
cannot have arbitrary amplitudes. Therefore, in the cal-
culations discussed below we have set a maximum value.
All these constraints have been added to the optimization
algorithm.

In order to implement these equations, we have used the
qutip code as a base [51, 52]. We have, however, not
employed the QOCT algorithms provided by this plat-
form (at the time of writing of this article), but used the
gradient, computed as in Eq. (17), to feed our own
QOCT code [53], that then utilizes a general purpose
function optimization algorithm: the Sequential Least-
Squares Quadratic Programming (SLSQP) algorithm [54]
as implemented in the NLopt library [55].
III. RESULTS

A. The GdW$_{30}$ molecular spin qudit

In order to explore the potential of QOCT for the control of spin qubits, we have chosen a system, GdW$_{30}$ [27, 37], which is both well characterized and relatively simple. The molecular structure of this polyoxometalate cluster is shown in Fig. 1. It hosts a single Gd$^{3+}$ ion and forms crystals with all molecules oriented in the same manner. In addition, magnetically diluted crystals can be grown by simply replacing Gd$^{3+}$ with Y$^{3+}$, which is chemically equivalent but diamagnetic. This allows enhancing spin coherence times up to 2 – 3 $\mu$s [37] while keeping the possibility of orienting the magnetic fields $\vec{B}$ and $\vec{b}$ along specific molecular axes. This molecule shows a hard magnetic axis along the main molecular axis $z$. Its static spin Hamiltonian can be well described by Eqs. (1), (2) and (3) with $S = 7/2$, $g = 2$, $D = 1281$ MHz and $E = 294$ MHz. The overall splitting of the $d = 8$ multiplet is smaller than 1 K, or 20.8 GHz, thus ensuring that adjacent level splittings lie within the reach of conventional EPR as well as of other microwave technologies. In all calculations discussed below, we have chosen the static magnetic field $\vec{B}$ to point in the $x$ direction (medium axis) and set $B = 0.15$ T. Under such conditions, the eigenstates of $\hat{H}_{\text{Zeeman}} + \hat{H}_{\text{Zeeman}}$ become close approximations to pure spin projections along $\vec{B}$. The time-dependent magnetic field $\vec{b}$ is perpendicular, and points in the $y$ direction (easy axis), thus inducing transitions between adjacent energy levels.

B. Transition implementation via monochromatic pulses

In this section, we discuss the manipulation of the GdW$_{30}$ spin using monochromatic pulses resonant with the set of allowed transitions mentioned above and shown in Fig. 1. As an illustration, we consider the application of $\pi$ pulses linking every two of these states. Fig. 2 (top) displays the transformation infidelities (i.e. $1 - |\langle \psi(t^\lambda_\pi)|k \rangle|^2$) as a function of the time $t^\lambda_\pi$ allocated to complete the operation, for the seven $|j\rangle \rightarrow |k = j + 1\rangle$ transitions. One can see that the error in the outcome state is reduced as $t^\lambda_\pi \rightarrow \infty$. In fact, from the logarithmic plot one may infer a quadratic behaviour:

$$1 - |\langle \psi(t^\lambda_\pi)|k \rangle|^2 = O((1/t^\lambda_\pi)^2). \tag{21}$$

It becomes clear that, in order to ensure a given fidelity, a minimum time (or, equivalently, a maximum amplitude) is required.

C. Optimization of state-to-state transitions

In this and the following section, we apply the QOCT methods described in section II to quantum operations on GdW$_{30}$ having different targets. First, we optimize resonant transitions and sequences of these. Then, we tackle the optimization of quantum gates. The goal here is to see how OCT permits to increase the fidelities shown in Fig. 2 (top), by allowing for the presence in the pulse of other frequencies, besides the resonant one. We have performed QOCT calculations [56] considering, for each transition, the same total propagation time used to create Fig. 2 (top). Each of these propagation times $t^\lambda_\pi$ corresponds to a $\pi$-pulse amplitude $\lambda$ [Eq. (21)], that we have used now to set a bound for the Fourier expansion coefficients in the OCT maximization: the temporal shape of the microwave field is given by Eq. 20, where

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig2}
\caption{Top: Infidelities of the seven main transitions in the GdW$_{30}$ molecule, as function of the $\pi$-pulse time. Bottom: Infidelities of the seven main transitions in the GdW$_{30}$ molecule, as function of the total pulse time, for pulses obtained with optimal control. Inset: Time-dependent shape of the pulses used to generate two of the seven transitions: one $\pi$-pulse (black), and one optimized pulse (red), corresponding to the thick black and red dots, respectively, on the pink lines.}
\end{figure}
Let us consider now the more general case of optimizing transitions between states, say \( |n\rangle \) and \( |m\rangle \), that are not directly coupled by the external field, i.e. \( \langle n | S_y | m \rangle = 0 \). A possible solution is to concatenate a series of \( \sigma \)-pulses, between intermediate states. In fact, this is a criterion for universality: if any two states can be connected through others, the qudit can perform any unitary and, in this sense, can be regarded as a universal quantum processor. However, the time needed is proportional to the number of pulses, which in practice is a limitation. Thus, in this case, QOCT offers a clear advantage by replacing a single shaped pulse to achieve, and accelerate, a process that would otherwise require a sequence of 7 monochromatic pulses.

In Fig. 3 we have tested this by comparing the infidelity in the transition \( |0\rangle \rightarrow |7\rangle \), using a sequence of \( \sigma \)-pulses between adjacent levels, \( |k\rangle \rightarrow |k+1\rangle \), and using QOCT. The improvement is quite significant. In particular, we have run over a range of amplitudes \( \lambda \), that determine the \( \sigma \)-pulse length for each transition, \( t_{\lambda}^j(k \rightarrow k+1) \). The full \( |0\rangle \rightarrow |7\rangle \) process then requires \( t_f = \sum_{k=0}^{6} t_{\lambda}^j(k \rightarrow k+1) \).

The plot displays the fidelity achieved with these pulse sequences. Then, for each of those times, we have performed QOCT calculations, once again setting a bound for the amplitudes of the individual Fourier terms equal to \( \lambda \). The plot shows how, even at very short operation times, the fidelities achieved by the optimized pulses are almost equal to one. In terms of time scales, a 99 % fidelity can be achieved in less than 10 ns, thus much shorter than \( T_2^\ast \simeq 2 \mu s \), while reaching the same result with a sequence of monochromatic pulses would take more than 1 \( \mu s \). In Fig. 3 we also show results of a similar calculation, but using the \( |0\rangle \rightarrow \frac{1}{\sqrt{2}}(|0\rangle - i|7\rangle) \) state as target, a superposition state that can be reached with a \( \pi/2 \)-pulse corresponding to the \( |0\rangle \rightarrow |1\rangle \) transition, followed by the same previous sequence of \( \pi \)-pulses that raises the state through the next adjacent levels. The results are qualitatively similar to the ones obtained for the full \( |0\rangle \) to \( |7\rangle \) transition, thus showing that the speed enhancement achieved by the application of QOCT is not restricted to any particular class of transitions. This allows targeting the optimization of complex gates, which is discussed next.

### D. Quantum gate optimization

Finally, we proceed to our true objective: the search for non-trivial pulse shapes that realize quantum gates, with high fidelities, in short times. As target gates, we have chosen the family of Deutsch gates \cite{57, 58}:

\[
D(\theta) = \begin{pmatrix}
I_6 & 0 & 0 \\
0 & i \cos(\theta) & \sin(\theta) \\
0 & \sin(\theta) & i \cos(\theta)
\end{pmatrix},
\]

where \( I_6 \) is the 6 \( \times \) 6 identity matrix. Note that this family includes the Toffoli gate, for \( \theta = \pi/2 \). The reason for focusing on this set of gates is that it is universal: any circuit can be constructed by combination of these components.

The total propagation time \( t_f \) has been set to 20 times the maximum natural period of the field-free Hamiltonian, i.e. the period corresponding to the smallest transition frequency. For the choice of static magnetic field used here (\( \vec{B} = 0.15 T \vec{e}_z \)), \( t_f \sim 10 \) ns.

As discussed above, the optimizations are performed constraining the allowed parameter set, such that each sinusoidal (or cosinusoidal) term in the expansion \cite{20} has a maximum amplitude, i.e.

\[
\frac{2 u_k}{\sqrt{t_f}} \leq b_{\text{max}}.
\]
FIG. 4. Optimal pulse in the time domain (top), and its power spectrum in the frequency domain (bottom), of the optimal pulse obtained for the $\theta = \pi/4$ Deutsch gate.

In the calculations shown here, we have set $b_{\text{max}}$ to a relatively high value of 20 mT in order to make the operation, and therefore also the computational, times manageable short. The influence of $b_{\text{max}}$ on $t_f$ is discussed below. The optimization algorithm is an iterative process that we stop when the quality of the gate, measured as $F(U(u; t_f)) = |\langle \hat{U}(u, t_f) \cdot \hat{D}(\theta) \rangle|^2$, reaches a certain threshold, that for these calculations we have set to 0.99.

Figure 4 displays the results obtained for $\theta = \pi/4$ as an example (the results obtained for other angles are qualitatively similar). The top panel shows $f(u(t); t)$ in real time, whereas the bottom panels display its power spectrum. Both plots demonstrate the complexity of the pulses, that do not have dominant frequencies.

In the previous example, we have set a total operation time $t_f$ and an amplitude bound $b_{\text{max}}$. Those magnitudes are of course related: if, for a given $t_f$, we set a too low amplitude bound, the quality of the gate (as measured by Eq. (14)) will also be too low. In fact, if we fix a threshold for acceptable gate quality (say, 0.99), for each given propagation time there will be a minimum amplitude bound necessary for the QOCT algorithm to return a successful pulse. Even with optimal pulse shapes, we need a minimum of field amplitudes in order to get a high quality gate. We have therefore studied this issue, computing the minimum amplitude bound that can be used to constrain the QOCT calculation in order to get a given gate, as a function of operation time. The results are shown in Fig. 5.

This type of plot helps to ascertain whether or not the gate operations are experimentally feasible, as in practice there is a hardware bound on the field amplitudes that can be used. Given this limit, one may learn from the plot what operation times are feasible, even with shaped optimal pulses. Obviously, the lower the available amplitudes, the longer the operations times must be.

IV. CONCLUSIONS

The previous results show that the use of complex pulses, engineered by optimal control techniques, provides a method for improving the speed of operations performed on spin qudits. The advantages are already noticeable for the realization of elementary transitions, when the application of monochromatic pulses is limited by the need of keeping the excitation amplitudes sufficiently low. Yet, they become even more important when dealing with more complex operations. Then, QOCT allows reaching any given fidelity of the outcome wave function with a single control pulse replacing the often long sequence of resonant pulses required by standard techniques. This possibility is especially relevant for algorithms that involve transitions between relatively disconnected states. For a necessarily limited coherence spin time, this difference can represent a big gain in the performance of such protocols.

The molecular qudit design and the way information is encoded on its spin states can be adapted to suit best the requirements of specific quantum protocols [18, 59], thus offering a vast choice of possible molecular platforms and implementations. Optimal control techniques described...
in this work are flexible enough to be made compatible with almost any of them. Although we have here considered a specific molecule for illustrative purposes, QOCT can deal with any spin model and with diverse control interactions (e.g., magnetic or electric field pulses). Therefore, it can be adapted to boost the implementation of diverse algorithms. We feel that it will be of special relevance to quantum error correction, because reaching a fidelity improvement with such protocols critically depends on the ratio between the implementation time and $T_2$. With an additional computational cost, one can even consider optimizing the control pulses to best compensate for the actual sources of decoherence in each molecule, mainly dephasing by nuclear spins located in the ligand shell surrounding the magnetic core.

The use of more sophisticated control pulses represents a challenge to experimental implementations. Most commercial EPR systems work with relatively narrow excitation bands and a reduced choice of pulse shapes. In recent years such systems have been complemented with waveguide generators able to arbitrarily design the excitation pulses [60–62]. Still, these set-ups are limited to frequencies lying sufficiently close to the cavity resonance frequency. In order to expand the frequency window, one can resort to on-chip circuits, with the excitation being driven by an open transmission line. This scheme, illustrated by Fig. 1, has been applied to investigate coherent control of NV centers in diamond [63] and to perform broadband spectroscopy of GdW$_{30}$ and other molecular spin qudits [22–27]. It can also be used to read out the outcome, either by looking at the frequency dependent absorption, in a projective measurement, or by coupling it to a superconducting resonator that can perform non-demolition, dispersive measurements of the qudit states [64]. Some experimental systems combining superconducting resonators and broadband control lines have been recently reported [65]. Another promising implementation is based on the combination of single-molecule electronics with gates or coils able to locally generate arbitrarily shaped electric or magnetic microwave pulses. Experiments performed on molecules trapped between point contacts or between a metal substrate and a STM tip have provided the first measurements of spin coherence in individual molecules [66] and achieved the realization of Grover’s search algorithm using three nuclear spin states in a Tb-based molecule [28].

In summary, the application of quantum optimal control theory to operate the states of molecular spin qudits offers remarkable prospects to improve their performance, compensating for their not too long coherence times. Equipped with these techniques, many more molecular systems and applications can become feasible, thus contributing to an alternative and promising path towards large scale quantum computation and simulation.

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processor with trapped ions (2021). arXiv:2109.06903 [quant-ph]

[12] S. Asaad, V. Mourik, B. Joecker, M. A. I. Johnson, A. D. Baczewski, H. R. Fingau, M. T. Madzik, V. Schmitt, J. J. Pla, F. E. Hudson, K. M. Itoh, J. C. McCallum, A. S. Dzurak, A. Laucht, and A. Morello, Coherent electrical control of a single high-spin nucleus in silicon. Nature 579, 205 (2020)

[13] M. Neeley, M. Ansmann, R. C. Bialczak, M. Hofheinz, S. Carretta, D. Zueco, A. Chiesa, ´A. G´omez-Le´ on, and A. Gaita-Ari˜ no, F. Luis, S. Hill, and E. Coronado, Molecular magnetization and related phenomena in molecular materials, Angewandte Chemie International Edition 42, 268 (2003)

[14] I. Gimeno, A. Urtizberea, J. Rom´an-Roche, D. Zueco, E. Moreno-Pineda, M. Damjanovi´c, O. Fuhr, W. Werns- als, Angewandte Chemie International Edition 42, 268 (2003)

[15] G. Aromi, D. Aguilà, F. Luis, S. Hill, and E. Coronado, Design of magnetic coordination complexes for quantum computing., Chem. Soc. Rev. 41, 537 (2012).

[16] M. Atzori and R. Sessoli, The second quantum revolution: Role and challenges of molecular chemistry, J. Am. Chem. Soc. 141, 11339 (2019).

[17] A. Gaita-Ariño, F. Luis, S. Hill, and E. Coronado, Molecular spins for quantum computation., Nature Chem. 11, 301 (2019).

[18] S. Carretta, D. Zueco, A. Chiesa, Á. Gómez-León, and F. Luis, A perspective on scaling up quantum computation with molecular spins, Applied Physics Letters 118, 240501 (2021)

[19] E. Moreno-Pineda, M. Damjanović, O. Fuhr, W. Wernsdorfer, and M. Ruben, Nuclear spin isomers: Engineering a tetrahedral spin qudit, Angewandte Chemie International Edition 56, 9915 (2017)

[20] E. Moreno-Pineda, C. Godfrin, F. Balestros, W. Wernsdorfer, and M. Ruben, Molecular spin qudits for quantum algorithms, Chem. Soc. Rev. 47, 501 (2018)

[21] R. Hussain, G. Alldi, A. Chiesa, E. Garlatti, D. Mitcov, A. Konstantatos, K. S. Pedersen, R. De Renzi, S. Piligkos, and S. Carretta, Coherent manipulation of a molecular ln-based nuclear qudit coupled to an electron qubit, Journal of the American Chemical Society 140, 9814 (2018).

[22] I. Gimeno, A. Urtizberea, J. Román-Roche, D. Zueco, A. Camón, P. J. Alonso, O. Roubeau, and F. Luis, Broadband spectroscopy of a vanadyl porphyrin: a model electronuclear spin qudit. Chem. Sci. , (2021).

[23] S. Chicco, A. Chiesa, G. Alldi, E. Garlatti, M. Atzori, L. Sorace, R. De Renzi, R. Sessoli, and S. Carretta, Controlled coherent dynamics of [vo(tpp)], a prototype molecular nuclear qudit with an ancilla. Chem. Sci. 12, 12046 (2021)

[24] F. Luis, A. Repollés, M. J. Martínez-Pérez, D. Aguilá, O. Roubeau, D. Zueco, P. J. Alonso, M. Evangelisti, A. Camón, J. Sesé, L. A. Barrios, and G. Aromí, Molecular prototypes for spin-based cnot and swap quantum gates., Phys. Rev. Lett. 107, 117203 (2011).

[25] D. Aguilá, D. Barrios, V. Velasco, O. Roubeau, A. Repollés, P. Alonso, J. Sesé, S. Teat, F. Luis, and G. Aromí, Heterodimetallic [lnln’ln] lanthanide complexes: Toward a chemical design of two-qubit molecular spin quantum gates., J. Am. Chem. Soc. 136, 14215 (2014).

[26] J. Ferrando-Soria, E. Moreno-Pineda, A. Chiesa, A. Fernández, S. A. Magee, S. Carretta, P. Santini, I. Vitorica-Yrezabal, F. Tuna, E. J. L. McIntness, and R. E. P. Winpenny, A modular design of molecular qudits to implement universal quantum gates., Nat. Commun. 7, 11377 (2016).

[27] M. D. Jenkins, Y. Duan, B. Diosdado, J. J. García-Ripoll, A. Gaita-Ariño, C. Giménez-Saiz, P. J. Alonso, E. Coronado, and F. Luis, Coherent manipulation of three-qubit states in a molecular single-ion magnet, Phys. Rev. B 95, 064423 (2017).

[28] C. Godfrin, A. Ferhat, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, and F. Balestro, Operating quantum states in single magnetic molecules: Implementation of grover’s quantum algorithm, Phys. Rev. Lett. 119, 187702 (2017).

[29] F. Luis, P. J. Alonso, O. Roubeau, V. Velasco, D. Zueco, D. Aguilà, J. I. Martínez, L. A. Barrios, and G. Aromí, A disymmetric [gdg] coordination molecular dimer hosting six addressable spin qudits as quantum simulators of light-matter interactions, J. Mater. Chem. C 9, 10266 (2021).

[30] A. Chiesa, E. Macaluso, F. Petiziol, S. Wimberger, P. Santini, and S. Carretta, Molecular nanomagnets as qudits with embedded quantum-error correction, The Journal of Physical Chemistry Letters 11, 8610 (2020).

[31] A. Chiesa, F. Petiziol, E. Macaluso, S. Wimberger, P. Santini, and S. Carretta, Embedded quantum-error correction and controlled-phase gate for molecular spin qudits, AIP Advances 11, 025134 (2021).

[32] C. Godfrin, R. Ballou, E. Bonet, M. Ruben, S. Klyatskaya, W. W., and F. Balestro, Generalized Ramsey interferometry explored with a single nuclear spin qudit, npj Quantum Inf. 4, 53 (2018).

[33] K. Bader, D. Dengler, S. Lenz, B. Endward, S.-D. Jiang, P. Neugebauer, and J. van Slageren, Room temperature quantum coherence in a potential molecular qubit, Nat. Commun 5, 5304 (2014).

[34] J. M. Zadrozny, J. Niklas, O. G. Poluektov, and D. E. Freedman, Millisecond coherence time in a tunable molecular electronic spin qudit., ACS Cent. Sci. 1, 488 (2015).

[35] M. J. Martínez-Pérez, S. Cardona-Serrà, C. Schlegel, F. Moro, P. J. Alonso, H. Prima-García, J. M. Clemente-Juan, M. Evangelisti, A. Gaita-Ariño, J. Sesé, J. van Slageren, E. Coronado, and F. Luis, Gd-based single-ion magnets with tunable magnetic anisotropy: Molecular design of spin qudits, Phys. Rev. Lett. 108, 247213 (2012).

[36] C. Brit, R. Chakraborti, and H. Rabitz, Control of quantum phenomena: past present and future, New Journal of Physics 12, 075008 (2010).

[37] J. P. Palao and R. Kosloff, Quantum computing by an optimal control algorithm for unitary transformations, Phys. Rev. Lett. 89, 188301 (2002).

[38] E. Brion, D. Comparat, and G. Harel, Implementation of a cnot gate in two cold rydberg atoms by the nonholo-
onomic control technique, The European Physical Journal D - Atomic, Molecular, Optical and Plasma Physics \textbf{38}, 381 (2006).

[41] S. Schirmer, Implementation of quantum gates via optimal control, Journal of Modern Optics \textbf{56}, 831 (2009).

[42] D. M. Reich, M. Ndong, and C. P. Koch, Monotonically convergent optimization in quantum control using krotov's method, The Journal of Chemical Physics \textbf{136}, 104103 (2012).

[43] S. Hou, L. Wang, and X. Yi, Realization of quantum gates by lyapunov control, Physics Letters A \textbf{378}, 699 (2014).

[44] Y. Chou, S.-Y. Huang, and H.-S. Goan, Optimal control of fast and high-fidelity quantum gates with electron and nuclear spins of a nitrogen-vacancy center in diamond, Phys. Rev. A \textbf{91}, 052315 (2015).

[45] K. Arai and Y. Ohtsuki, Reduced-dynamics approach for optimally designing unitary transformations, Phys. Rev. A \textbf{92}, 062302 (2015).

[46] D. Dong, C. Wu, C. Chen, B. Qi, I. R. Petersen, and F. Nori, Learning robust pulses for generating universal quantum gates, Computer Physics Communications \textbf{183}, 1760 (2012).

[47] J. Johansson, P. Nation, and F. Nori, Qutip: An open-source python framework for the dynamics of open quantum systems, Computer Physics Communications \textbf{183}, 1234 (2013).

[48] G. de Lange, Z. H. Wang, D. M. Notley, V. V. Dobrovitski, R. Hanson, Universal dynamical decoupling of a single solid-state spin from a spin bath, Science \textbf{330}, 60–63 (2010).

[49] Alvaro Gómez-León, F. Luis, and D. Zueco, Dispersive readout of molecular spin qudits (2021), arXiv:2109.14639 [quant-ph].

[50] S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben, and W. Wernsdorfer, Electrically driven nuclear spin resonance in single-molecule magnets, Science \textbf{344}, 1135 (2014).

[51] J. Johansson, P. Nation, and F. Nori, Qutip: An open-source python framework for the dynamics of open quantum systems, Computer Physics Communications \textbf{183}, 1760 (2012).

[52] J. Johansson, P. Nation, and F. Nori, Qutip 2: A python framework for the dynamics of open quantum systems, Computer Physics Communications \textbf{184}, 1234 (2013).

[53] A. Castro \textit{et al.}, qocttools, \url{https://acbarrigon.gitlab.io/qocttools/}.

[54] D. Kraft, Algorithm 733: Tomp–fortran modules for optimal control calculations, ACM Trans. Math. Softw. \textbf{20}, 262–281 (1994).

[55] S. G. Johnson, The nlopt nonlinear-optimization package, http://github.com/stevengj/nlopt.

[56] Note that the OCT for the simpler problem of state population – in contrast to the harder problem of the creation of a given evolution operator or gate – requires equations that are slightly different to the ones described in section II.

[57] D. E. Deutsch and R. Penrose, Quantum computational networks, Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences \textbf{425}, 73 (1989).

[58] X.-F. Shi, Deutsch, toffoli, and cnot gates via rydberg blockade of neutral atoms, Phys. Rev. Applied \textbf{9}, 051001 (2018).

[59] F. Petziol, A. Chiesa, S. Winberger, P. Santini, and S. Carretta, Counteracting dephasing in molecular nanomagnets by optimized qudit encodings, npj Quantum Information 7, 10.1038/s41534-021-00466-3 (2021).

[60] M. Tsitlin, R. W. Quine, G. A. Rinard, S. S. Eaton, and G. R. Eaton, Digital epr with an arbitrary waveform generator and direct detection at the carrier frequency, J. Mag. Res. \textbf{213}, 119 (2011).

[61] P. E. Spindler, P. Schöps, A. M. Bowen, B. Endeward, and T. F. Prisner, Shaped pulses in epr, in eMagRes (John Wiley & Sons, Ltd, 2016) pp. 1477–1492, https://onlinelibrary.wiley.com/doi/pdf/10.1002/9780470034590.emrstm1520.