

CONTROL OF THE MOLECULAR ALIGNMENT OR ORIENTATION BY LASER PULSES

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We review the motivations and recent theoretical and experimental progress in laser alignment or orientation of molecules in space. We present a method to produce field free aligned or oriented linear molecules using a succession of short laser pulses. The problem of orienting molecules is an example of a unitary control problem in a Hilbert space with infinite dimension. The originality of our method relies on a precise construction of oriented quantum target states which maximize the orientation in finite dimensional subspaces. Orientation at zero temperature (pure state control) and of molecular thermal ensemble (mixed state control) are investigated.

1. Introduction — Motivations

The problem of controlling the alignment or orientation of molecules in space has attracted a fair amount of attention in the field of molecular physics and chemical physics. In this introduction, we present the motivations for such studies and, and give some account of the progress.

First of all, we must define what we call molecular alignment and orientation. In classical terms, aligning a molecular axis in space means to bring an axis fixed in the molecular frame to a given fixed direction in the laboratory frame. Orienting the molecule means that in addition to aligning, we require that the orientation of the axis be fixed in the laboratory frame. This last definition makes sense only if the molecule is not symmetric with respect to a reflection on a plane orthogonal to the molecular axis we like to orient. For instance, aligning a $A - B$ linear molecule to a vertical axis (in the laboratory frame) means to bring the axis joining the two atoms A

and B to a vertical position. Orienting the molecule means that in addition we require for instance that A is up and B down. In the quantum world we are only allowed to speak in the sense of probability. We can define an angular probability distribution $P(\theta, \phi)$ where (θ, ϕ) are the spherical angles (co-latitude and azimuthal angle, respectively) locating the molecular axis with respect to the fixed laboratory frame axis. $P(\theta, \phi)d\Omega$ gives the probability to find the molecular axis in the $d\Omega = \sin\theta d\theta d\phi$ solid angle centered on the (θ, ϕ) position. We can consider a molecule as aligned if its angular probability distribution is mainly supported near $\theta = 0$ and/or $\theta = \pi$. If in addition $P(\theta, \phi)$ is mainly supported in the upper space only ($\theta \in [0, \frac{\pi}{2}]$ and $\phi \in [0, 2\pi]$ for instance), we consider the molecule to be oriented.

1.1. Motivations

Why molecular alignment and orientation are important? In the following, three examples in different areas of investigation are presented where the control of the molecular alignment and/or orientations is a crucial point.

- (1) **Stereochemistry.** Stereochemistry is the study of the influence of the relative orientation of atoms and molecules on the outcomes of a chemical reactions. To our knowledge, this is the first motivation to produce aligned or oriented molecule. Indeed, this idea goes back to the 1960s, when the first molecular beam machines were built, to produces inelastic or reactive collisions. The development of the field of molecular beam chemistry and reaction dynamics in the 1960s [1] invited direct experimental study of the steric effect. The objective of those experiments is to control the relative orientation of the reagent and to measure its influence on the reaction probability. Several strategies have been applied to produces oriented or aligned beams of molecules whose presentation is deferred to the next section.
- (2) **Femtosecond optics.** Nowadays the production of laser pulse with a duration of about 10-100 femtosecond ($1 \text{ fs} = 10^{-15}$) can be achieved almost routinely in laboratory. Researchers would like to control precisely the amplitude and phase of such pulses for practical applications and also to compress them to sub-femtosecond durations. One line of investigation is based on the propagation of the laser pulse in a medium of oriented molecules. The main idea is that carefully controlled molecular rotational dynamics induces periodic change in the refractive index of the propagation media, then inducing controlled phase and amplitude variation of the laser pulse [2, 3].

- (3) **High harmonic generation and molecular ionization.** When an atom or a molecule is irradiated with an intense (intensity about $10^{14} - 10^{15}$ W/cm²) infrared (wavelength $\simeq 800$ nm) laser pulse, the molecule can be ionized and can also emit coherent X-UV attosecond light pulses. The accurate understanding of these processes requires the alignment or orientation of the irradiated molecule. Furthermore, recent experiments are exploring the possibility of reconstructing the initial quantum electronic molecular state (molecular state tomography) by observing the emitted light or the angular distribution of emitted electrons [4–8]. Those experiments need carefully aligned or oriented molecules.

1.2. *Experimental methods*

In this section, we give a brief survey of the methods that have been used in laboratory to align or orient molecules. The first experiment with oriented molecules was realized in 1965 by Kramer and Bernstein [1]. They used an axially symmetric hexapole electrostatic field to focus molecular beams. Symmetric top-like molecules traveling through the inhomogeneous electric field of the hexapole follow sinusoidal trajectories and focus at a certain point, depending on their rotational quantum state and the voltage on the hexapole rods (see [9] for a detailed description of the technique). This technique allows to obtain molecular beams in a given rotational state which can be oriented. In fact, in these types of experiments, it is the molecule angular momentum which is directly oriented and not the molecular axis.

Next, in the 1990s a “brute force orientation technique” was introduced by Loesh and Remscheid [10] and independently by Friedrich and Herschbach [11]. This technique made it possible to carry out experiments on oriented molecules not being symmetric tops as was necessary for applying hexapole state selection method. This technique relies on the application of an intense electrostatic field on rotationally very cold polar molecules obtained in supersonic beams. The anisotropy of the Stark effect allows molecules in the lowest few rotational states to be trapped in “pendular states” and thereby confined to librate (oscillate about the field axis) over a limited angular range.

In 1995, Friedrich and Herschbach [12] showed that an intense and non resonant laser field is able to align a molecule, with respect to the polarization of the laser electric vector, through the interaction between the oscillating laser field and the induced molecular dipole moment. The induced

dipole moment results from the interaction of the laser field through the molecular anisotropic polarizability. The induced dipole moment interaction can be described by a potential energy term $V(\theta) \propto \cos^2 \theta$ where θ is the angle between the molecular axis and the laser electric field vector. This potential presents a symmetric double-well with minima at $\theta = 0$ and $\theta = \pi$. Because of the fast oscillations of the electric field this technique cannot orient the molecule; it only produces alignment. The lower energy levels correspond to the so called pendular aligned states. Later in 1999, Friedrich and Hershbach proposed [13] to combine an electrostatic field with the laser field to achieve molecular orientation in addition to alignment. The pendular level induced by the laser field comes in nearly degenerate tunneling doublet states of opposite parity. If the molecule is polar, the introduction of a static electric field couples the two components of a doublet, inducing tunneling and thus orientation. This idea has been implemented by Sakai *et al.* recently [14]. At the same time another scheme was proposed by Dion *et al.* [15] and refined by Guerin *et al.* [16]. It consists in using two lasers with different frequencies ω and 2ω and different phases. An experimental confirmation was performed by Ohmura *et al.* in 2004 [17].

All those schemes rely on a slow switching of the laser, inducing an adiabatic passage from a pure rotational state of the free molecule to an aligned or oriented pendular state of the molecule interacting with the field. The alignment or orientation can then be maintained while the molecule is interacting with the laser field. But the alignment and orientation is completely destroyed when the laser field is switched off adiabatically. This has the drawback that the intense laser field can modify the physics and/or the chemistry and can constitute an obstacle in some applications which require free oriented molecules.

Hence, researchers have begun to focus on pulsed schemes which is the opposite of the adiabatic case, the objective being to produce free (non interacting) aligned or oriented molecules during sufficiently long time. The first experimental demonstration of post pulse alignment was achieved by Rosca-Pruna and Vrakking [18], and was followed by several other groups (for a review see [19]). In these experiments a short laser pulse interacts through the molecular polarizability, and creates a coherent superposition of rotational eigenstates. Constructive interference of the component in the wave packet, and thus alignment, occur shortly after the pulse and repeat periodically in time. The molecular alignment can be detected by a sudden dissociation of the molecule, in that case the angular distribution of the fragments reveals the alignment of the parent molecule. The

molecular alignment can also be detected by non destructive spectroscopic methods [20, 21]. These non-adiabatic schemes are interesting for applications of aligned molecules because it enables alignment under field free conditions. For alignment based on a single short laser pulse, stronger alignment of a molecular sample is obtained by increasing the pulse intensity. This approach is limited by saturation of the alignment itself, or by the requirement that alignment pulse intensity must be kept below a threshold corresponding to unwanted processes such as dissociation or ionization of the molecule. The idea to use a train of laser pulses to control the molecular alignment was first proposed by Averbukh and Arvieu [22, 23]. The goal is to obtain better alignment or orientation efficiency with a lower laser intensity in each pulse.

In this article we will attempt to summarize recent results concerning the control of orientation or alignment of linear molecule by a train of laser pulses. These results have been obtained in the collaboration between the author and O. Atabek, D. Daems, C. M. Dion, S. Guerin, H. Jauslin and D. Sugny [24–27]. The chapter is organized as follows: In section 2, we present the model used to describe the molecule and its interaction with the laser pulses. Section 3 is devoted to the control problem. We first try to formalize the controls objectives and show how to build target quantum states that corresponds to an aligned or oriented molecule. Then, we show strategies to reach these target states with a train of laser pulses. Two cases are envisaged: the control of a pure state, where the molecule can be considered initially in the ground states (zero temperature). And the control of a mixed state, where the molecule is initially in a mixed state describing a thermal ensemble. Finally, we end with a conclusion and some prospects.

2. The Model

2.1. *The free molecule*

We consider a linear molecule as a rigid rotor. This is of course an approximation, because a molecule posses many other degree of freedom than the rotational one: electronic motion and vibrational motion which correspond in general to higher frequency modes. These other degrees of freedom can be safely ignored if we can consider that the molecule remains in its ground electronic an vibrational quantum state. In our case, this implies that the laser frequency used for the control is not equal to a transition energy between theses modes.

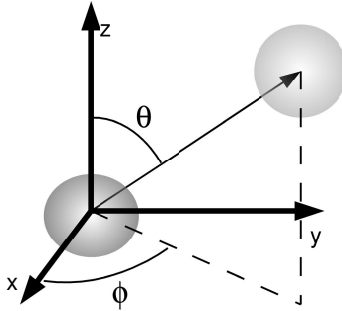


Fig. 1. Spherical angles defining the rotor position in space.

The position of the linear molecule in space is given by the spherical angles (θ, ϕ) where θ is the co-latitude and ϕ the azimuthal angle (see Fig. 1). The Hamiltonian of the free molecule corresponds to the rotational kinetic energy:

$$H_0 = BJ^2 \quad (2.1)$$

where B is the rotational constant which is related to the inertia moment I of the molecule by $B = \frac{1}{2I}$. $J^2 = J_x^2 + J_y^2 + J_z^2$, where $J_i (i = x, y, z)$ are the components in the laboratory frame of the angular momentum operator. The eigenvectors $|j, m\rangle$ of $H = BJ^2$ can be chosen as eigenstates of J_z with eigenvalues m (H_0 does not depend on ϕ). We have :

$$\begin{aligned} J^2|j, m\rangle &= j(j+1)|j, m\rangle, \\ J_z|j, m\rangle &= m|j, m\rangle, \end{aligned} \quad (2.2)$$

with $j \in \mathbb{N}$ and $-j \leq m \leq +j$. To a rotor energy $E_j = Bj(j+1)$ corresponds $2j+1$ degenerated quantum states. In the (θ, ϕ) representation the eigenvectors are represented by spherical harmonics: $\langle \theta, \phi | j, m \rangle = Y_{j,m}(\theta, \phi)$ and the Hamiltonian is the spherical Laplacian:

$$H_0 = B \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right], \quad (2.3)$$

defined on the Hilbert space $\mathcal{H} = L^2(\mathbb{S}^2)$.

The evolution operator $U_0(t, t_0)$, solution of the Schrödinger equation:

$$i \frac{\partial}{\partial t} U_0(t, t_0) = H_0 U_0(t, t_0); \quad U(t_0, t_0) = \mathbb{1}, \quad (2.4)$$

which is periodic in t with period $T_{\text{rot}} = \frac{\pi}{B}$. T_{rot} is called the rotational period.

2.2. Molecule-laser interaction

2.2.1. Dipole moment interaction

If the molecule is not symmetric, it can interact with light through its permanent dipole moment $\vec{\mu}$. In that case the interaction Hamiltonian is given by:

$$V_{\mu} = -\vec{\mu} \cdot \vec{E}(t) = \mu E(t) \cos \theta, \quad (2.5)$$

where $\vec{E}(t) = E(t)\vec{e}_z$ is the laser electric field which we consider as linearly polarized in the z direction. The laser electric field is written as

$$E(t) = \mathcal{E}(t) \cos \omega t, \quad (2.6)$$

where ω is the laser angular frequency and $\mathcal{E}(t)$ is the pulse envelope with a typical duration τ . The propagation of a light pulse in vacuum requires that

$$\int_{-\infty}^{\infty} E(t) dt = 0. \quad (2.7)$$

In a typical laser pulse, the duration τ is much longer than the carrier period $T_L = \frac{2\pi}{\omega}$, as a consequence the electric field is almost symmetric in space. It is clear that such a laser pulse cannot orient a molecule. It has been shown [28, 29] that it is possible to generate very special pulses, called half-cycle pulses, with a duration of the order of picosecond (10^{-15} s), with a very highly non symmetric shape. This pulse shape can be divided into two parts: The first part of the pulse is short and the amplitude of the electric field can reach a large value. The time integral of the electric field corresponding to this first part is not zero giving us the possibility to orient the molecule. On the contrary, the second part of the pulse takes a longer time but with a very low electric field, such that Eq. (2.7) is fulfilled. The effect of this second part of the pulse on the molecule can be safely neglected [30].

2.2.2. Polarizability interaction

If the molecule is symmetric (a homonuclear diatomic molecule for instance) it cannot possess a permanent dipole moment. But the interaction with the laser field can polarize the molecular electronic cloud giving rise to an induced dipole moment: $\vec{\mu}(t) = \overset{\leftarrow}{\alpha} \vec{E}(t)$ where $\overset{\leftarrow}{\alpha}$ is the molecular polarizability second rank tensor. For a linear molecule the induced $\vec{\mu}$ can be decomposed into the sum of a component parallel to the molecular axis:

$\mu_{\parallel} = \alpha_{\parallel} E_{\parallel}$ and an orthogonal component: $\mu_{\perp} = \alpha_{\perp} E_{\perp}$. The interaction of the laser field with this induced dipole moment gives the interaction potential: $V(t) = -\vec{\mu}(t) \cdot \vec{E}(t) = -(\overleftarrow{\alpha} \vec{E}(t)) \cdot \vec{E}(t)$. For a linear molecule, it becomes: $V(t) = -\alpha E^2(t) \cos^2 \theta - \alpha_{\perp} E^2(t)$, where $\alpha = \alpha_{\parallel} - \alpha_{\perp}$. In the case where the laser pulse duration is long compared to the carrier period T_L [31, 32] and to the rotational period T_{rot} , an effective interaction operator can be obtained by averaging $V(t)$ over the period T_L . In this way we obtain the interaction Hamiltonian:

$$V_{\alpha}(t) = -\alpha \mathcal{E}^2(t) \cos^2 \theta - \alpha_{\perp} \mathcal{E}^2(t), \quad (2.8)$$

where only the laser pulse envelope plays a role. For a symmetric molecule, only alignment makes sense, it is clear that such interaction in principle can also align the molecule.

The time-dependent Hamiltonian describing the molecule interacting with the laser field can be written as:

$$H(t) = H_0 + V_{\mu(\alpha)}(t). \quad (2.9)$$

2.3. Molecular states time dependent evolution

The evolution operator for the interacting molecule is the solution of the Schrödinger equation:

$$\frac{\partial}{\partial t} U(t, t_0) = [H_0 + V_{\mu(\alpha)}(t)] U(t, t_0); \quad U(t_0, t_0) = \mathbb{1}.$$

We note that the Hamiltonian (and the evolution operator) does not depend on ϕ thus the quantum number m is conserved during the evolution.

We now consider two different cases depending on the initial molecular state.

2.3.1. Pure state

We first consider the case where the molecular initial state is a pure state, for instance if the temperature is low enough to ensure that only the ground rotational state of the molecule is populated. In this case the initial state is an element $|\psi(t_0)\rangle \in \mathcal{H}$ and its evolution from time t_0 to t is given by

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle. \quad (2.10)$$

If O is an observable, *i.e.* a self adjoint operator on \mathcal{H} , then we define the expectation $\langle O \rangle(t)$ of O in the state $|\psi(t)\rangle$ at time t as

$$\langle O \rangle(t) = \langle \psi(t) | O \psi(t) \rangle. \quad (2.11)$$

2.3.2. Mixed state

For most molecules it requires very low temperature (less than 1 K) to ensure that only the ground rotational state is populated. We thus consider also the case where the initial state of the molecule is in a statistical superposition of rotational states. In that case, the initial state at time t_0 can be described by the density operator $\rho(t_0)$ which is a self adjoint positive operator on \mathcal{H} , with $\text{tr}[\rho(t_0)] = 1$. For an initial thermal ensemble at temperature T the density operator is given by

$$\rho(t_0) = (\text{tr}[e^{-\beta H_0}])^{-1} e^{-\beta H_0}, \quad (2.12)$$

where $\beta = \frac{1}{kT}$ and k is the Boltzmann constant.

The time evolution of ρ from time t_0 to time t is given by

$$\rho(t) = U(t, t_0)\rho(t_0)U^{-1}(t, t_0), \quad (2.13)$$

we see that the evolution is unitary. We note that the spectrum of $\rho(t)$ is conserved during such an evolution, and that an initial mixed state remains mixed during the evolution; it cannot be converted to a pure state.

The expectation $\langle O \rangle(t)$ of an observable O in state $\rho(t)$ at time t is given by

$$\langle O \rangle(t) = \text{tr}[\rho(t)O]. \quad (2.14)$$

2.3.3. Sudden approximation

We consider short laser pulses, such that the pulse duration τ is very small compared to the rotational period T_{rot} . This condition is routinely achieved in laboratory. Indeed typical molecular rotational periods are of the order of several picoseconds and laser durations less than 100 femtoseconds are now easily achievable. In that case, it can be shown [33, 34] that the evolution operator $U(t, t_0)$, solution of Eq. (2.3), can be factored as

$$\begin{aligned} U(t > \tau, 0) &\simeq e^{-iH_0 t} e^{i\mathcal{V}_{\mu(\alpha)}} \\ &= U_0(t, 0)U_V, \end{aligned}$$

where we have defined

$$\mathcal{V}_{\mu(\alpha)} = \int_{-\infty}^{+\infty} V_{\mu(\alpha)}(t') dt', \quad (2.15)$$

more precisely,

$$\begin{aligned}\mathcal{V}_\alpha &= \left[\alpha \int_{-\infty}^{+\infty} \mathcal{E}^2(t') dt' \right] \cos^2 \theta \equiv \mathcal{A}_\alpha \cos^2 \theta, \\ \mathcal{V}_\mu &= \left[\mu \int_{-\infty}^{+\infty} \mathcal{E}(t') \cos \omega t' dt' \right] \cos \theta \equiv \mathcal{A}_\mu \cos \theta.\end{aligned}\quad (2.16)$$

2.4. Alignment or orientation characterization

To quantify the degree of molecular orientation or alignment two measures are used.

2.4.1. Orientation

The molecular orientation will be characterized by the expectation $\langle \cos \theta \rangle$. A perfect orientation is achieved if $|\langle \cos \theta \rangle| = 1$. Here $\cos \theta$ is considered as an operator on \mathcal{H} , and its matrix representation in the basis of free molecular eigenstates $|j, m\rangle$ is tridiagonal. It can be written as

$$\cos \theta = \sum_{j, |m| \leq j} C_{j,m} [|j+1, m\rangle \langle j, m| + |j, m\rangle \langle j+1, m|], \quad (2.17)$$

with $C_{j,m} = \left[\frac{(j+1)^2 - m^2}{(2j+1)(2j+3)} \right]^{\frac{1}{2}}$. We note that free molecular eigenstates $|j, m\rangle$ are not oriented: $\langle j, m | \cos \theta | j, m \rangle = 0$.

2.4.2. Alignment

To characterize the degree of molecular alignment, we use the expectation $\langle \cos^2 \theta \rangle$. For free molecular rotational states $\langle j, m | \cos^2 \theta | j, m \rangle \neq 0$ in particular $\langle j=0, m=0 | \cos^2 \theta | j=0, m=0 \rangle = \frac{1}{3}$.

3. Control

3.1. Control objectives

Our goal is to maximize the orientation or the alignment of the molecule, more precisely we want to find a laser field such that the expectation $\langle \cos \theta \rangle(t_f)$ or $\langle \cos^2 \theta \rangle(t_f)$ reaches its maximum value for some finite time t_f . In addition, we impose that at time t_f when the orientation (or alignment) reaches its maximum value the molecule has to be free, that is $E(t_f) = 0$. This condition ensures that experiments using such oriented molecules will not be perturbed by the orienting laser field. Furthermore, we would like

to obtain an oriented (or aligned) molecule during long enough time. The maximum achieved value for the orientation (or alignment) will be called *efficiency* of the control. The time during which the orientation (alignment) takes high enough value will be called *persistence*.

To show that indeed a control is necessary, we first compute the evolution of the orientation $\langle \cos \theta \rangle(t)$ as a function of time t , after the interaction with a single short pulse. The results of such a computation are presented in

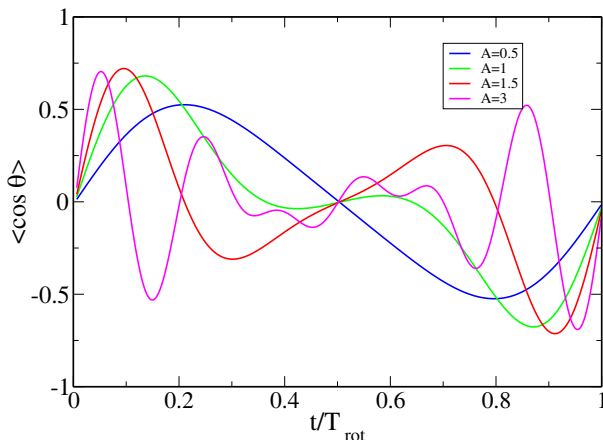


Fig. 2. $\langle \cos \theta \rangle$ as a function of time in units of the rotational T_{rot} period, for 4 values of the amplitudes of the radiative coupling $\mathcal{A}_\mu = 0.5, 1, 1.5, 3$. The initial state is the ground state $|j = 0, m = 0\rangle$ and a single pulse interacts with the molecule at time $t = 0$.

Fig. 2, for four values of the radiative coupling \mathcal{A}_μ (see Eq. (2.16)). We note that increasing \mathcal{A}_μ first increases the maximum value reached by $\langle \cos \theta \rangle$, but value of \mathcal{A}_μ higher than 1.5 does not increase any longer the value of $\langle \cos \theta \rangle$. Orientation higher than $\langle \cos \theta \rangle = 0.7$ cannot be reached with such an intense single pulse. Furthermore, the increase of the radiative coupling causes a decrease of the persistence. Indeed, if we take as a measure of the persistence the time during which the value of $\langle \cos \theta \rangle$ is higher than 0.5, we see that increasing \mathcal{A}_μ from 1 to 3 decreases the persistence by a factor of 3. This can be explained, by the fact that increasing the radiative coupling increases the kinetic energy transferred to the molecule, inducing fast rotation of the molecule.

In conclusion, to obtain good orientation during long enough time, a single intense pulse is not sufficient. An alternative idea is to use a sequence of short pulses and to optimize the delay and intensities of such pulses.

In the sudden approximation the evolution operator corresponding to a sequence of N short laser pulses at time t_n ($n = 0, 1, 2, \dots, N - 1$) can be written as

$$U(t > t_{N-1}, 0) = e^{-iH_0(t-t_N)} \prod_{n=0}^{N-1} e^{iH_0(t_{n+1}-t_n)} e^{i\mathcal{A}_n \cos \theta}. \quad (3.1)$$

We have at hand, $N - 1$ time delays ($t_{n+1} - t_n$) and N amplitudes \mathcal{A}_n , as control parameters that can be optimized to achieve our objective.

But before we describe the control strategy, we first will define target states that maximize the expectation $\langle \cos \theta \rangle$. Then in a second step we look for laser pulse sequences that bring the molecule from their initial state to the target state. We first consider the control for pure states and then we envisage the case of mixed states.

3.2. Control at zero temperature — Pure state control

3.2.1. Target states

Zero temperature means that the initial state of the molecule is simply the ground state $|\psi_0\rangle = |j = 0, m = 0\rangle$. Because the evolution is unitary, the state remains pure during the time evolution. Furthermore, the z-axis angular momentum projection m being conserved its value remains $m = 0$. Thus, we look for a state $|\chi\rangle \in \mathcal{H}$ which maximizes $\langle \chi | \cos \theta | \chi \rangle$. But the maximum value of $\langle \cos \theta \rangle$ is 1, and the state that realizes this bound is not physically acceptable. It is not a smooth function of θ , or in other words it corresponds to a molecule with an infinite kinetic rotational energy.

To define physically acceptable target states we proceed as follows. We define the finite dimensional Hilbert $\mathcal{H}^{(j_{\max})}$ as the complex linear span of $\{|j, m = 0\rangle; j = 0, 1, 2, \dots, j_{\max}\}$. We look for the state $|\chi^{(j_{\max})}\rangle \in \mathcal{H}^{(j_{\max})}$ which maximizes $\langle \chi^{(j_{\max})} | \cos \theta | \chi^{(j_{\max})} \rangle$. This state, which we call the *target state* is simply the eigenvector of $\cos \theta^{(j_{\max})}$ with the highest eigenvalue $\lambda^{(j_{\max})}$, where $\cos \theta^{(j_{\max})}$ is the restriction of the operator $\cos \theta$ in the $\mathcal{H}^{(j_{\max})}$ finite Hilbert space. Of course this target state depends on the chosen dimension j_{\max} for the $\mathcal{H}^{(j_{\max})}$ Hilbert space. We can choose the value of j_{\max} so that the target state corresponds to a suitable oriented molecule. In Fig. 3, we present the angular probability distribution $P(\theta, \phi)$ defined as

$$P(\theta, \phi) = \left| \langle \theta, \phi | \chi^{(j_{\max})} \rangle \right|^2 = \left| \sum_{j=0}^{j_{\max}} \langle j, m = 0 | \chi^{(j_{\max})} \rangle Y_{j,0}(\theta, \phi) \right|^2, \quad (3.2)$$

as a function of θ for three values of j_{\max} , $j_{\max} = 1, 3$ and 5 . A good surprise is that a very well oriented state is obtained with low value of j_{\max} . Indeed, the orientation expectation values $\langle \cos(j_{\max}) \theta \rangle$ obtained in each case are: $\langle \cos(j_{\max}) \theta \rangle = 0.57, 0.86$ and 0.96 , respectively.

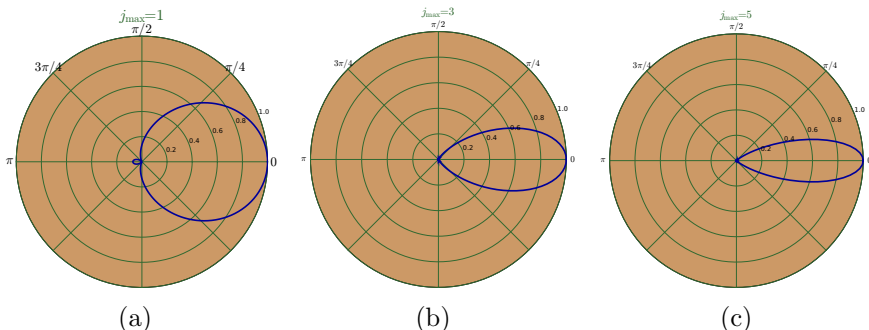


Fig. 3. Angular probability density $P(\theta, \phi = 0)/P(0)$ in polar coordinate for the target state (see Eq (3.2)) as a function of θ , for three value of j_{\max} . (a) $j_{\max} = 1$, (b) $j_{\max} = 3$ and (c) $j_{\max} = 5$.

To evaluate the orientation persistence of these target states we have systematically calculated the free evolution of these target state $|\chi^{(j_{\max})}(t)\rangle = U_0(t, 0)|\chi^{(j_{\max})}\rangle$ and computed their orientation expectation $\langle \cos \theta \rangle(t) = \langle \chi^{(j_{\max})}(t) | \cos \theta | \chi^{(j_{\max})}(t) \rangle$ as a function of time. In Fig. 4 the time evolution of $\langle \cos \theta \rangle(t)$ is presented for $j_{\max} = 1, 3, 5$. As we have noted previously, we see that as j_{\max} increases the persistence decreases. But for $j_{\max} = 5$ the orientation remains greater than $\langle \cos \theta \rangle = 0.5$ during more than than 10% of the rotational period, this can correspond to several picoseconds for a usual molecule. In Fig. 5, we present the target states efficiency and persistence for values of j_{\max} ranging from $j_{\max} = 1$ to $j_{\max} = 12$. The persistence is defined as the time during which the orientation remains greater than $\langle \cos \theta \rangle = 0.5$. We see clearly in this figure that while j_{\max} increases, the orientation increases but the persistence decreases. To choose the value of j_{\max} , a compromise must be made. We choose $j_{\max} = 5$ as a good compromise. The same method for building target states for the alignment control purpose can be applied, by replacing $\cos \theta$ by $\cos^2 \theta$. We are confident that the same approach can also be applied to other control problems in an infinite dimensional Hilbert space, where the goal is to maximize the expectation of an observable. We emphasize that this way of determining the target state does not depend on the characteristics of the molecule.

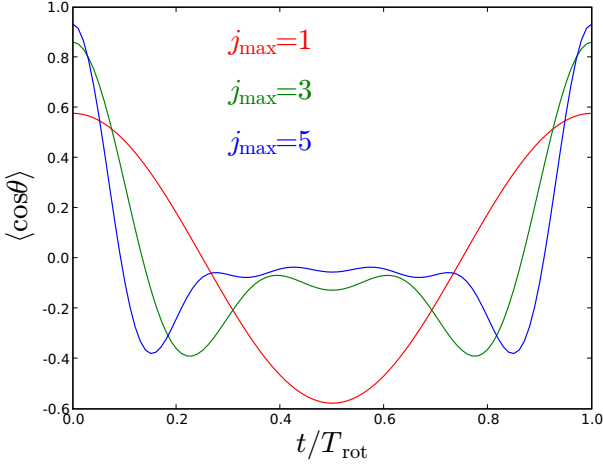


Fig. 4. $\langle \cos \theta \rangle(t)$ as a function of time, for 3 target states corresponding to the value of $j_{\text{max}} = 1, 2, 3$. The initial state is the corresponding target state and the evolution is the free evolution computed with $U_0(t, 0)$.

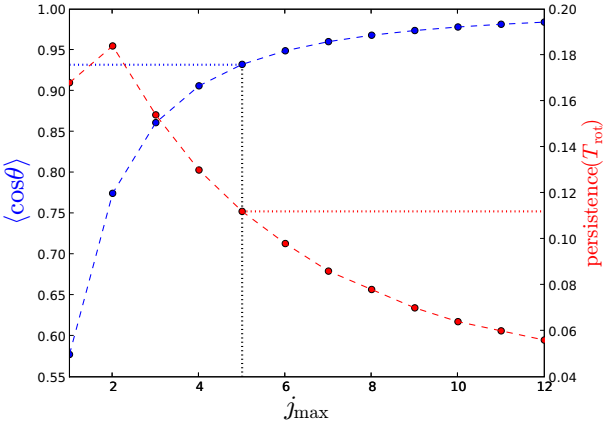


Fig. 5. Target states orientation $\langle \cos \theta \rangle$ (in blue and left vertical axis) and persistence (in red and right vertical axis) as a function of j_{max} . The persistence is defined as the time during which the orientation remains greater than $\langle \cos \theta \rangle = 0.5$, and is given in unit of the rotational period T_{rot} .

Now that we have precisely determined the target state, we want to find a control strategy to reach this target state from the molecular ground state.

3.2.2. Open questions

Before we discuss any details of the strategies used to control the orientation, we present some open questions that are both of mathematical and physical interest. At first sight, in our context, the control objective can be formulated as:

For a given target $|\chi^{(j_{\max})}\rangle$, is it possible to find two finite sequences, τ_n and \mathcal{A}_n , such that

$$\left| \left\langle \chi^{(j_{\max})} \left| \prod_{n=0}^{N-1} e^{-iH_0\tau_n} e^{i\mathcal{A}_n \cos\theta} \right| j = 0 \right\rangle \right| = 1.$$

This might be too demanding. Indeed, the infinite dimensionality of the Hilbert space \mathcal{H} makes it very difficult to achieve such a task. We can reformulate the objective in the following less demanding way:

For a given target state $|\chi^{(j_{\max})}\rangle$ and for a given ϵ , are there two finite sequences, τ_n and \mathcal{A}_n , such that

$$1 - \left| \left\langle \chi^{(j_{\max})} \left| \prod_{n=0}^{N-1} e^{-iH_0\tau_n} e^{i\mathcal{A}_n \cos\theta} \right| j = 0, m = 0 \right\rangle \right| < \epsilon.$$

If the answer to this question is positive, then we can further ask: how many kicks are needed to reach the target state within ϵ .

Because, we do not have answer to these questions we must proceed by doing numerical experiments.

3.2.3. Strategy of maxima

This strategy consists in applying a laser pulse each time $|\langle \chi^{(j_{\max}=5)} | \psi(t) \rangle|$ reaches a global maximum over a rotational period. In Fig. 6, we present the evolution of $|\langle \chi^{(j_{\max}=5)} | \psi(t) \rangle|^2$ as a function of time t , under such strategy. We see that after ten laser pulses the target state is almost reached. The target state is not exactly reached because of the infinite dimensional nature of the Hilbert space. To evaluate the robustness of this strategy, we have made calculations with different laser amplitudes $\mathcal{A}_o \pm 20\%$ but with the same time delays. The numerical results are presented in Fig. 7, showing that this strategy is indeed robust.

3.2.4. Optimization with an evolutionary algorithm

For experimental applications, the control of more than 2 or 3 pulses becomes a difficult task. Hence, we look for a solution with only two laser

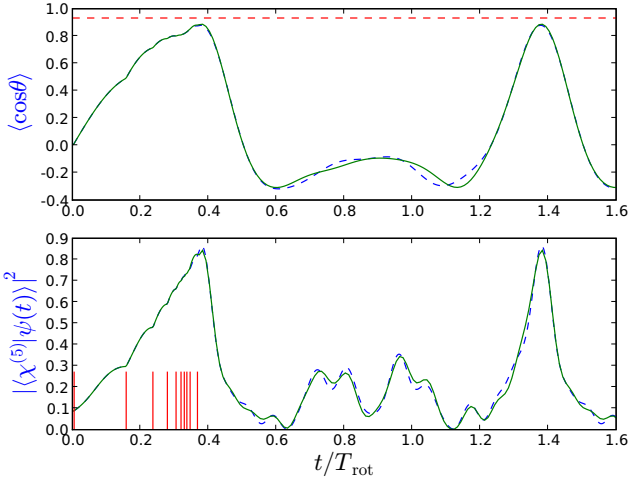


Fig. 6. Strategy of maxima. Bottom panel: $|\langle \chi^{(j_{\text{max}}=5)} | \psi(t) \rangle|^2$ as a function of time t in unit of rotational period T_{rot} . Top panel: $\langle \cos \theta \rangle(t)$; the horizontal dashed line represent the value of $\langle \chi^{(j_{\text{max}}=5)} | \cos \theta \chi^{(j_{\text{max}}=5)} \rangle$. The dashed line corresponds to numerical calculation in the 6 dimensional Hilbert space $\mathcal{H}^{(j_{\text{max}}=5)}$. The solid line corresponds to calculation in a higher dimensional space. The initial state is $|j = 0, m = 0\rangle$. A pulse is applied each time $|\langle \chi^{(j_{\text{max}}=5)} | \psi(t) \rangle|^2$ reaches a global maximum over a rotational period. The laser amplitude $\mathcal{A}_o = 1$ for all pulses and ten pulses are used.

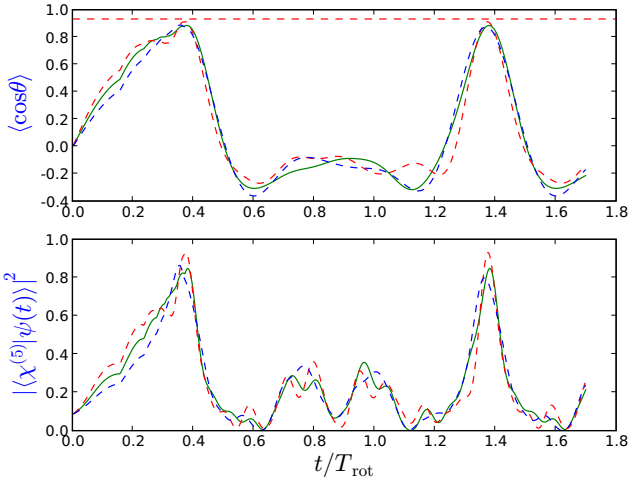


Fig. 7. Robustness. Same calculation as Fig. 6 but with different laser amplitudes \mathcal{A}_o . Solid green line same as Fig. 6, $\mathcal{A}_o = 1$. Dashed red line $\mathcal{A}_o = 1.2$. Dashed blue line $\mathcal{A}_o = 0.8$.

pulses, and optimize the delay and laser amplitudes in order to maximize $\sup_{t \in [0, T_{\text{rot}}]} |\langle \chi^{(j_{\text{max}}=5)} | \psi(t) \rangle|^2$. The optimization was done with an evolutionary algorithm. The result is presented in Fig. 8, which shows that a very satisfactory solution is obtained. Indeed, the target state is almost reached, the maximum value being $|\langle \chi^{(j_{\text{max}}=5)} | \psi(t) \rangle|^2 = 0.9887$ with pulses amplitudes given by $\mathcal{A}_o = 0.9741, 3.2930$ and a time delay between the two pulses equal to $0.2419 \times T_{\text{rot}}$. The orientation reaches almost its maximal value in $\mathcal{H}^{(j_{\text{max}}=5)}$ Hilbert space. In conclusion, we have successfully found

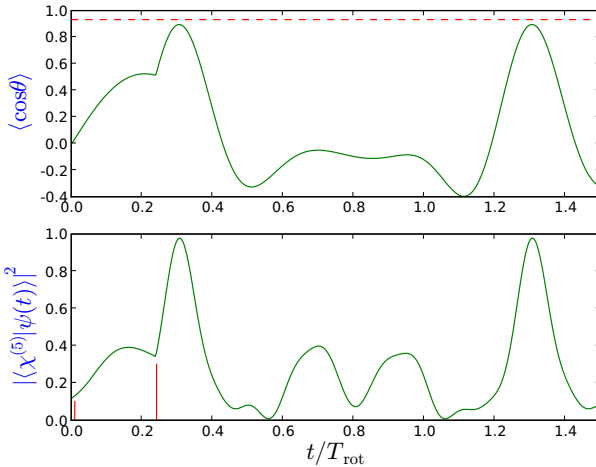


Fig. 8. Time evolution of the orientation (top) and $|\langle \chi^{(j_{\text{max}}=5)} | \psi(t) \rangle|^2$ (bottom) with two laser pulses, where time delay and amplitudes has been optimized. The horizontal line represent the highest orientation value reachable in the $\mathcal{H}^{(j_{\text{max}}=5)}$ Hilbert space.

a very simple solution to the problem of orienting a linear molecule at zero temperature, with only two laser pulses. The steps to find this solution was:

- Define a finite dimensional Hilbert space where the dynamic is approximated.
- Define a target state space which maximize our objective in this finite dimensional Hilbert space.
- Find a strategy to reach the target state from the initial state.

The problem is that in current laboratory experiments, the temperature is higher than the rotational energy, hence molecules cannot be considered as being initially in their ground state. In the next section we will see how to adapt the present scheme for a non zero temperature.

3.3. Control of a thermal ensemble — Mixed state control

We now consider a thermal ensemble initially described by the following density operator ρ_0 :

$$\rho_0 = \frac{1}{Z} e^{-\beta H_0} = \frac{1}{Z} \sum_{j=0}^{\infty} \sum_{m=-j}^{+j} e^{-\beta B j(j+1)} |j, m\rangle \langle j, m|, \quad (3.3)$$

where

$$Z = \text{tr} [e^{-\beta H_0}] = \sum_{j=0}^{\infty} (2j+1) e^{-\beta B j(j+1)} \quad (3.4)$$

and $\beta = \frac{1}{kT}$ with k being the Boltzmann constant.

The eigenvalues of ρ_0 given by $\frac{1}{Z} e^{-\beta B j(j+1)}$ are $(2j+1)^{\text{th}}$ degenerated, since they do not depend on m . Hence, the finite $\mathcal{H}^{(j_{\max})}$ Hilbert space that we will use to define the target states is now defined as the linear span of $\{|j, m\rangle; j = 0, 1, 2, \dots, j_{\max} \text{ and } |m| < j\}$. The dimension of $\mathcal{H}^{(j_{\max})}$ is given by: $N_{j_{\max}} = \sum_{j=0}^{j_{\max}} \sum_{m=-j}^j 1 = (2j+1)^2$. We note that contrary to the zero temperature case the minimal dimension $N_{j_{\max}}$ required to represent accurately our system will be determined by the temperature T .

3.3.1. Target states

As for the zero temperature case we look for a state ρ_{opt} which maximizes $\langle \cos \theta \rangle$ in the space $\mathcal{H}^{(j_{\max})}$. But now ρ_{opt} is a density operator and the expectation $\langle \cos \theta \rangle$ is given by $\langle \cos \theta \rangle = \text{tr} [\rho_{\text{opt}} \cos \theta]$. We also require that ρ_{opt} must be reachable from the initial state ρ_0 . This implies that ρ_{opt} must be unitarily equivalent to ρ_0 ; *i.e.* there exists a unitary operator U in $\mathcal{H}^{(j_{\max})}$ such that $\rho_{\text{opt}} = U^{-1} \rho_0 U$. Hence, ρ_{opt} has the same spectrum as ρ_0 . The density operator ρ_{opt} fulfilling these properties is represented by a diagonal matrix in the eigenbasis of the $\cos \theta^{(j_{\max})}$ operator, and can be written as [35]

$$\rho_{\text{opt}} = \sum_{n=1}^{N_{j_{\max}}} |\chi_n\rangle \omega_n \langle \chi_n|, \quad (3.5)$$

with $\omega_1 \leq \omega_2 \leq \dots \leq \omega_N$ being the eigenvalues of ρ_0 ($\omega_n = \frac{1}{Z} e^{-\beta B j_n(j_n+1)}$) ordered in the same way as the eigenvalues $\chi_1 \leq \chi_2 \leq \dots \leq \chi_N$ corresponding to eigenvectors $|\chi_n\rangle$ of $\cos \theta^{(j_{\max})}$.

One problem remains, *i.e.*, ρ_{opt} is in fact not reachable from ρ_0 with the dynamics induced by the $U(t, t_0)$ evolution operator, indeed $U(t, t_0)$ cannot

change the quantum number m . We have taken care about the kinematical constraint $\rho_{\text{opt}} = U^{-1}\rho_0U$, but we have not taken into account the dynamical constraint coming from the specific chosen dynamics, which involves linear polarized laser pulses. To take into account this constraint, we split the $\mathcal{H}^{(j_{\text{max}})}$ Hilbert space as $\mathcal{H}^{(j_{\text{max}})} = \bigoplus_{m=-j_{\text{max}}}^{m=j_{\text{max}}} \mathcal{H}_m^{(j_{\text{max}})}$ where each $\mathcal{H}_m^{(j_{\text{max}})}$ is the linear span of $\{|j, m\rangle; j = |m|, |m|+1, |m|+2, \dots, j_{\text{max}}\}$. Correspondingly, the target state can be written as $\rho_t^{(j_{\text{max}})} = \bigoplus_{m=-j_{\text{max}}}^{m=j_{\text{max}}} \rho_m^{(j_{\text{max}})}$ where each $\rho_m^{(j_{\text{max}})}$ is a density operator defined in the same way as ρ_{opt} by Eq. (3.5) but in $\mathcal{H}_m^{(j_{\text{max}})}$. Physically, we may say that ρ_{opt} corresponds to an optimal state where the laser polarization has not been specified and ρ_t corresponds to the target state that can be reached with a linear polarized laser.

As for the zero temperature case we can calculate the efficiency and persistence of these target states as a function of j_{max} (see Fig. 5). The results for a temperature $T = 5$ K and a rotational constant B such that $\beta B = 5$ which corresponds to the LiCl molecule, are presented in Fig. 9. In this figure, we see that contrary to the zero temperature case, higher j_{max} 's are needed to achieve a good orientation, and consequently with a lower persistence. Nevertheless, with $j_{\text{max}} = 6$ we obtain $\langle \cos \theta \rangle = 0.7$ and a

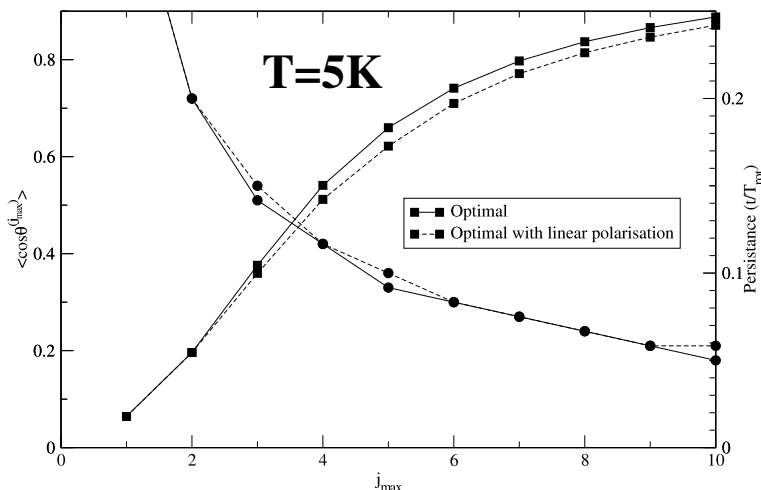


Fig. 9. Orientation (squares and left vertical axis) and persistence (circles and right vertical axis) in unit of rotational period as a function of j_{max} for the optimal target states ρ_{opt} (solid line) and the target states ρ_t (dashed line) corresponding to a linear polarized laser. The temperature is $T = 5$ K and $\frac{B}{kT} \simeq 0.2$.

persistence of $0.08T_{\text{rot}}$ which is satisfactory. Another surprising result is that the efficiency and persistence corresponding to ρ_{opt} and ρ_t are almost the same. This implies that considering linear polarized laser pulses is enough for our purpose; we cannot achieve better orientation with anymore complex polarization scheme. We emphasize that this result has been obtained without any dynamical simulation, but just by a detailed characterization of the target states. The effect of the temperature on the orientation of the

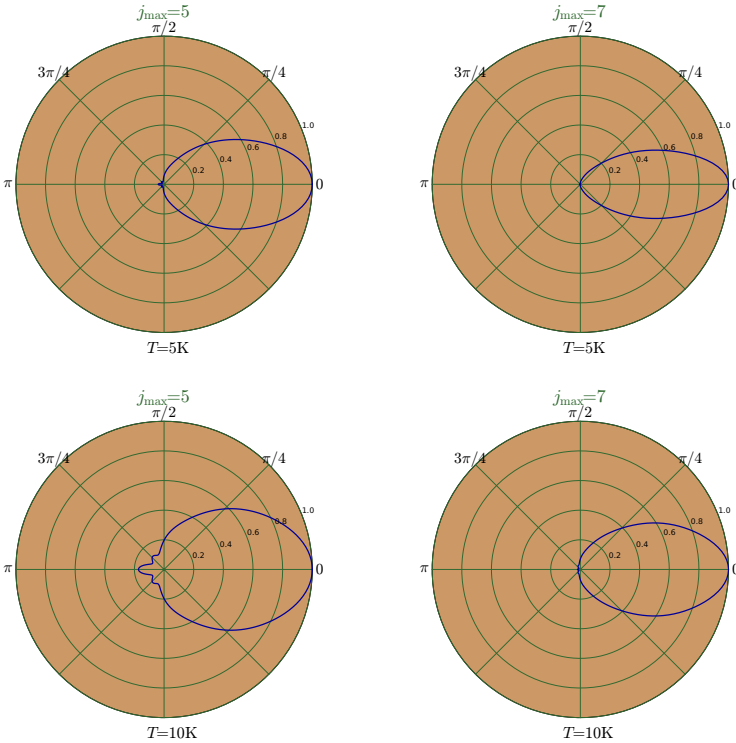


Fig. 10. Target states angular probability distributions for 2 temperatures $T = 5$ K (top), $T = 10$ K (bottom) and for $j_{\text{max}} = 5$ (left) and $j_{\text{max}} = 7$ (right).

target states can be seen in Fig. 10, where we have plotted the angular probability distribution $P(\theta, \phi = 0)$ for two temperatures $T = 5$ K and $T = 10$ K, $P(\theta, \phi)$ being defined as:

$$P(\theta, \phi) = \sum_{jm, j'm'} Y_{jm}^*(\theta, \phi) Y_{j'm'}(\theta, \phi) \langle j, m | \rho_t | j', m' \rangle. \quad (3.6)$$

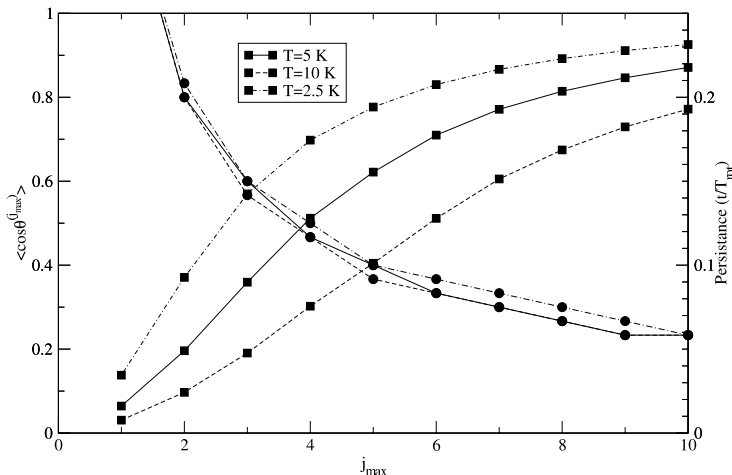


Fig. 11. Efficiency (square and left axis) and persistence (circle and right axis) in unit of T_{rot} for the target states ρ_t as a function of j_{\max} for three temperatures: $T = 2.5$ K (dashed line), $T = 5$ K (solid line) and $T = 10$ K (dashed-solid line). We see here that as in the case of zero temperature, the efficiency increases and the persistence decreases when j_{\max} increases. Furthermore, we note that the efficiency decreases with the temperature but that the persistence, if defined as the time during which the orientation remains higher than half its maximal value, does not depend on the temperature.

We have studied numerically the efficiency and persistence of target states as a function of j_{\max} and temperature, for a molecule like LiCl where $B \simeq 1$ K. The results are presented in Fig. 11. They show that, as in the case of zero temperature, the orientation increases and the persistence decreases when j_{\max} increase. In addition, we see that the orientation decreases when the temperature increases but the persistence almost does not depend on the temperature. Here the persistence has been defined as the time during which the orientation remains at half of its maximum value.

We have to concede that at high temperature it is nearly impossible to orient a thermal ensemble of linear molecules under unitary evolution; low temperature is required. The possibility to implement non unitary evolution (dissipative evolution) will be discussed in the conclusion section. Nevertheless, for a molecule such as LiCl at temperature $T = 5$ K ($\beta B = 0.2$), which is feasible in laboratory using a molecular supersonic beam, we can choose as a good compromise between orientation and persistence the target state corresponding to $j_{\max} = 6$. Indeed, this gives us an orientation $\langle \cos \theta \rangle \simeq 0.7$ and a persistence of $0.08 \times T_{\text{rot}}$.

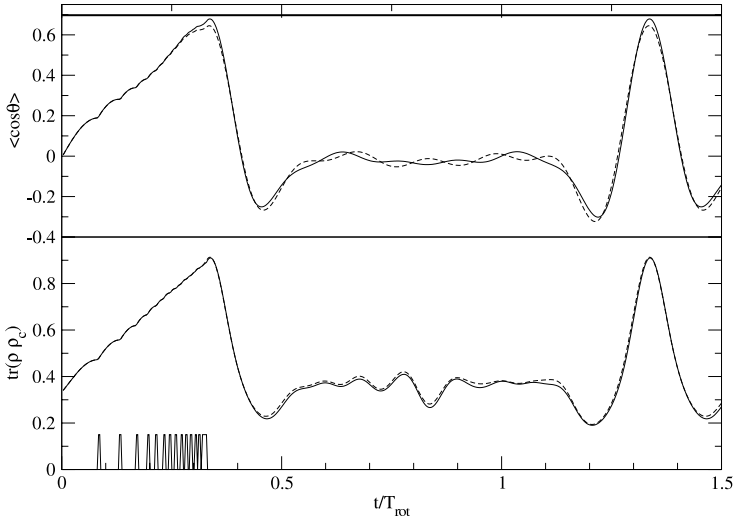


Fig. 12. Strategy of maxima. $\langle \cos \theta \rangle$ (top) and $\frac{\text{tr}[\rho(t)\rho_c^{j_{\max}=6}]}{\|\rho_c\|^2}$ (bottom) as a function of time in units of the rotational period T_{rot} . The thick horizontal line indicate the optimal value $\langle \cos \theta \rangle$ in $\mathcal{H}^{j_{\max}=6}$. Instants at which short laser pulses occur are indicated in the bottom panel. The temperature is $T = 5$ K. The molecule is LiCl with a rotational constant such that $\beta B \simeq 0.2$. The dashed line corresponds to an evolution calculated in the restricted Hilbert space $\mathcal{H}^{(j_{\max}=6)}$ and the solid line is for an evolution in a higher dimensional Hilbert space. We have taken care of comparing the time propagation in the restricted Hilbert space $\mathcal{H}^{(j_{\max})}$ and in a higher dimensional Hilbert space. The two evolutions are very similar thus showing that states outside $\mathcal{H}^{(j_{\max})}$ plays only a minor role.

3.3.2. Strategy of maxima

We apply the same strategy of maxima that we have used in the zero temperature case. The distance between the system actual state $\rho(t)$ and the target state ρ_c is evaluated using the Frobenius norm $\|A\| = \sqrt{\text{tr}[A^\dagger A]}$, where A^\dagger is the adjoint of A . $\|\rho\|^2$ is also called purity of the system when ρ is a density matrix. Because under unitary evolution the purity is conserved, it is equivalent to consider the “overlap” $S(t) = \frac{\text{tr}[\rho(t)\rho_c]}{\|\rho_c\|^2}$ as a measure of distance between $\rho(t)$ and ρ_c . Hence, we apply the strategy which consists in applying a laser pulse each time the free evolution of $S(t)$ reaches a global maximum over a rotational period. The results of such strategy are shown in Fig. 12, for a temperature of $T = 5$ K for the LiCl molecule and with the target state corresponding to $j_{\max} = 6$. We see that the target state is almost reached with 15 pulses with equal amplitudes $\mathcal{A}_0 = 1$.

4. Conclusion

We have presented a general method to control the alignment or orientation of a molecule by successive laser pulses. This control problem corresponds to a unitary control of pure or mixed states in an infinite dimensional Hilbert space. The originality of the method relies on a precise definition of target states which represent the objectives of the control. These target states are defined in a finite dimensional Hilbert space. As a consequence, the controlled dynamics that bring the initial state to one target state must restrict approximatively the system evolution in a finite dimensional space, with good accuracy. We think that this works with molecular rotational states, mainly because the energy spacing increases linearly when the state energy increases. It would be interesting to investigate if the method presented here can be applied to other systems or other degrees of freedom, which do not possess such a property.

The method presented here to orient molecule relies on the use of terahertz coherent pulses, the so called half cycle pulses [28, 29]. Until now, no experimental implementation of this scheme has been realized, which might be due to the difficulty to produce and manipulate such pulses. Recently, Sugarawa *et al.* [36] have proposed a method to orient molecule which combines the adiabatic and the pulsed method. The oriented state is reached by switching on adiabatically the laser field in the presence of a static field, but the laser is then switched off suddenly (in less than 200 fs). This method allows to obtain field-free oriented molecules. This theoretical proposal has been demonstrated experimentally by Goban *et al.* [37].

We have presented only the unitary control problem. We have shown that even with complex polarization scheme, very cold molecular ensembles are needed to obtain well oriented molecules. This is due to the fact that thermal mixed oriented target states are less oriented than pure target states, and that the unitary evolution cannot transform a pure state to a mixed state. It is natural then to investigate the non-unitary control problem. Physically, we can think of a molecule interacting with a gas buffer or in a liquid. The first attempt to address the molecular alignment or orientation dissipative control is due to Ramakrishna and Seideman [38–40]. The generalization of the method presented here to build target states in the case of dissipative control has been done by D. Sugny *et al.* [41]. The conclusion is that the presence of the dissipative medium is an obstacle to the orientation. It is not possible to purify the molecular state if the interaction with the dissipative medium is not controlled.

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