Efficient and long-lived field-free orientation of molecules by a single hybrid short pulse

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We show that a combination of a half-cycle pulse and a short nonresonant laser pulse produces a strongly enhanced postpulse orientation. Robust transients that display both efficient and long-lived orientation are obtained. The mechanism is analyzed in terms of optimal oriented target states in finite Hilbert subspaces and shows that hybrid pulses can prove useful for other control issues.

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Laser controlled processes such as molecular alignment and orientation are challenging issues that have received considerable attention both theoretically and experimentally. Whereas strong nonresonant adiabatic pulses can exhibit efficient alignment and orientation only when the pulse is on, linear polar molecules can be oriented under field-free conditions after the extinction of a short half-cycle pulse (HCP). Its highly asymmetrical temporal shape imparts a sudden momentum kick through the permanent dipole moment of the molecule, which orients it. This extends the use of a permanent static field (combined with pulsed nonresonant laser fields). Similarly to the alignment process by a nonresonant short pulse (measured by \( \langle \cos^2 \theta \rangle \) with \( \theta \) the angle between the axis of the molecule and the polarization direction of the laser field), the orientation by a HCP (measured by \( \langle \cos \theta \rangle \)) increases as a function of the field amplitude until it reaches a saturation at \( \langle \cos \theta \rangle \approx 0.75 \), which corresponds to an angle \( \cos^{-1}(\cos \theta) \approx 41^\circ \). Overcoming this saturation has been theoretically proved with the use of trains of laser pulses (HCP kicks) in the case of alignment (orientation).

Another crucial point, that has received less attention so far, is the duration during which the orientation is above a given threshold, which one would like to keep as long as possible. An important step made in was to establish a priori the two oriented target states (of opposite direction) in a given finite subspace generated by the lowest rotational states. These target states are optimal in the sense that they lead respectively to the maximum and minimum values of \( \langle \cos \theta \rangle \) in this given subspace. The choice of a suitable small dimension of the subspace allows one to generate an oriented target state of relatively long duration. The identification of such an optimal target state opens in particular the possibility to use standard optimization procedures (see e.g. [12]).

One of the main challenges consists now in reaching an optimal target state in a subspace of low dimension, characterizing a long-lived and efficient orientation, by a simple external field in a robust way and to ensure the persistence of this effect with respect to thermal averaging of finite temperature. We propose in this Letter a process that possesses such properties. By superimposing a pump laser field to a half-cycle pulse, we show that the maximal orientation reached after the pulse is significantly beyond the one induced by an HCP, and that it displays furthermore a longer duration. We obtain in particular the saturation \( \langle \cos \theta \rangle \approx 0.89 \), which corresponds to the angle \( \cos^{-1}(\cos \theta) \approx 27^\circ \). This efficient and long-lived orientation is obtained by adjusting only two parameters: the amplitudes of the laser and HCP fields. We obtain robust regions of the parameters generating this orientation.

We show that this process allows one to approach an optimal target state in one step. Under the action of a single hybrid pulse, the number of rotational states that are significantly populated remains finite and controllable. This generates a finite dimensional subspace in which an optimal target state can be constructed. When the dimension of this subspace increases, the associated optimal state yields a higher orientation efficiency while its duration decreases. By choosing appropriate intensities of the pump laser field and of the half-cycle pulse, we can both select and reach the target state with the desired efficiency and duration.

We consider a linear molecule in its ground vibronic state described in the 3D rigid rotor approximation. The effective Hamiltonian including its interaction with a HCP simultaneously combined with a pump laser field of respective amplitudes \( \mathcal{E}_{\text{HCP}}(t) \) and \( \mathcal{E}_L(t) \) is given by

\[
H_{\text{eff}}(t) = B L^2 - a_{\text{HCP}}(t) \cos \theta - a_L(t) \cos^2 \theta, \tag{1}
\]

where \( B \) is the rotational constant, \( a_{\text{HCP}} = \mu_0 \mathcal{E}_{\text{HCP}} \) with \( \mu_0 \) the permanent dipole moment, and \( a_L = \Delta \alpha \mathcal{E}_L^2 / 4 \) with \( \Delta \alpha \) the polarisability anisotropy. Note that \( \Delta \alpha \) is positive for linear molecules, which gives positive values for \( a_L \), whereas the sign of \( a_{\text{HCP}} \) is determined by the sign of the HCP amplitude \( \mathcal{E}_{\text{HCP}} \). The dynamics of
the system is readily determined with the help of the propagator in the impulsive regime, where the duration \( \tau \) of the pulse is much smaller than the rotational period \( \tau_{\text{rot}} = \pi \hbar / B \). For the process we suggest here, in the dimensionless time \( \tau = t / \tau_{\text{rot}} \) whose origin coincides with the extinction time of the pulse, the propagator reads \( U(s, 0) = e^{-i s \tau_{\text{rot}}} e^{i A_{\text{HCP}} \cos \theta e^{-i A_{L} \cos \theta}} \). The parameters \( A_{\text{HCP}} = \frac{1}{2} \int dt a_{\text{HCP}}(t) \) and \( A_{L} = \frac{1}{2} \int dt a_{L}(t) \) are respectively the total dimensionless areas of the HCP amplitudes and of the laser intensity.

We first consider the case of a cold molecule whose state after the pulse reads \( |\phi(s)\rangle = U(s, 0)|j = 0\rangle \) where \( |j\rangle \) stands for the spherical harmonics \( Y_{j}^{m} \) with \( m = 0 \). The orientation is measured by the expectation value \( \langle \cos \theta(s) \rangle = \langle \phi(s)| \cos \theta \phi(s) \rangle \). It is well-known that it is a periodic function (of unit period), which exhibits peaked revivals corresponding to molecular orientation along the field direction \( \mathbf{E} \).

\[ A_{\text{HCP}} = 1.25 \text{ and } A_{L} = 3.7 \text{ indicates that it is also possible to overcome the above saturation by combining an HCP of intensity slightly above unity with a laser pulse of high intensity.} \]

The direction of the orientation can be chosen by the sign of the amplitude of the HCP. Expressing the observable in terms of the projections \( c_{j} = \langle j|\phi(0)\rangle \) of the wave function right after the pulse onto the rotational states \( |j\rangle \) leads to \( \langle \cos \theta \rangle (s) = \frac{1}{2} \sum c_{j}^{*} c_{j+1} e^{-2i(j+1)\phi} + \text{c.c.} \). The coefficients \( c_{j} \) can be calculated for the above propagator in the approximation \( \langle j|\cos \theta| j \pm 1 \rangle \approx 1 / 2 \) which is more accurate for \( j \gg 0 \) (one has \( \langle 0|\cos \theta| 1 \rangle \approx 0.58, \langle 0|\cos \theta| 2 \rangle \approx 0.52, \langle 2|\cos \theta| 3 \rangle \approx 0.51, \cdots \)). This shows that the sign of each product \( c_{j}^{*} c_{j+1} \), and hence of \( \langle \cos \theta \rangle \), changes with the sign of \( A_{\text{HCP}} \). For positive \( A_{\text{HCP}} \), the expectation value corresponding to \( \text{max}_{s} \langle \cos \theta \rangle \) is positive on the island and negative on the plateau. We show below that the high orientation efficiency obtained in the region along the line \( A_{\text{HCP}} = 2.5 A_{L} \) has the remarkable property to approach very closely an optimal state as defined in \[10], which combines orientation of high efficiency and of long duration.

![FIG. 1: (Color online) Numerical contour plot of \( \text{max}_{s} \langle \cos \theta \rangle \) as a function of the total (dimensionless) areas \( A_{L} \) and \( A_{\text{HCP}} \). The straight line \( A_{\text{HCP}} = 2.5 A_{L} \) approximately indicates the maximum for given \( A_{\text{HCP}} \).](image1)

The maximal field-free orientation is displayed in Fig. 1 by plotting the maximum of \( \langle \cos \theta \rangle \) reached over a period as a function of the total areas \( A_{L} \) and \( A_{\text{HCP}} \) at zero rotational temperature, calculated with the above propagator. The case of a single HCP coincides with the ordinate axis. In the absence of the laser pulse it is seen that the maximal orientation saturates to a value of \( \langle \cos \theta \rangle \approx 0.75 \). In the presence of a simultaneous pump laser pulse, one observes a wide two-dimensional plateau as well as an island which are both associated with an orientation much higher than the saturation limit of a single high intensity HCP. The plateau is relatively flat in a large two-dimensional region centered approximately around the line \( A_{\text{HCP}} = 2.5 A_{L} \), implying that one can robustly reach a high efficiency for the orientation with a moderate HCP intensity. The island observed around \( A_{\text{HCP}} = 2.5 A_{L} \) seen in

![FIG. 2: As a function of \( A_{\text{HCP}} \), for \( A_{L} = A_{\text{HCP}} / 2.5 \), upper panel: (i) \( \text{max}_{s} \langle \cos \theta \rangle \) (solid line, right axis); (ii) for comparison, same quantity with \( A_{L} = 0 \) (dotted line); (iii) duration \( \Delta \) for which \( \langle \cos \theta \rangle > 0.5 \) (dashed line, left axis); Lower panels: square modulus \( P_{N} = |\langle \chi^{(N)}|\phi(\text{max})\rangle|^{2} \) of the projection of the state at the time giving the maximum of \( \langle \cos \theta \rangle \) on the optimal state \( |\chi^{(N)}\rangle \) (solid line, right axis); dimension \( N \) of the corresponding subspace (step function, left axis).](image2)
This shows that the saturation of $\langle \cos \theta \rangle \approx 0.75$ obtained with the HCP alone is significantly overcome (up to $\langle \cos \theta \rangle \approx 0.89$) when the HCP is associated with the laser of appropriate area. The upper frame of Fig. 2 also illustrates the duration of the orientation defined as the time during which $|\langle \cos \theta \rangle| \geq 0.5$ (see also Fig. 3). It is seen that the duration of the revival can be as large as about 18% of the rotational period. The properties displayed in Fig. 2 are robust with respect to the parameters $A_{\text{HCP}}$ and $A_L$ which need not be in a strict 2.5 ratio.

The efficiency of the obtained oriented state and its large duration are explained in terms of an optimal state as defined in [10]. We recall that the optimal states correspond to the two states that respectively minimize and maximize the projection of $\cos \theta$ in the finite subspace $H_N$ spanned by the $N$ lowest rotational states $|0\rangle, |1\rangle, \ldots, |N-1\rangle$, namely $\cos(N) \theta = \Pi_N \cos \theta \Pi_N$ with the projector $\Pi_N = \sum_{j=0}^{N-1} |j\rangle\langle j|$. Considering a finite subspace yields an operator that has a discrete spectrum, whose eigenvectors are readily calculated and for which the duration of the orientation provided by these states can be computed. Furthermore, the controllability of the system can be completely analyzed. For a given dimension $N$, the two optimal states are the eigenvectors associated respectively with the smallest and the largest eigenvalues of $\cos(N) \theta$. In the approximation $\langle j| \cos \theta |j \pm 1\rangle \approx 1/2$ one obtains

$$\langle \chi^{(N)}_\pm \rangle \approx \sqrt{\frac{2}{N+1}} \sum_{j=0}^{N-1} (-1)^{j+1} \sin \left( \pi \frac{j+1}{N+1} \right) |j\rangle,$$

giving the approximate optimal orientation

$$\langle \chi^{(N)}_\pm | \cos(N) \theta | \chi^{(N)}_\pm \rangle \approx \pm \cos \left( \frac{\pi}{N+1} \right).$$

The (relative) duration $\Delta$ of the orientation is defined as the time during which $|\langle \cos \theta \rangle| \geq \gamma$ for the revival of maximum efficiency, with $\gamma$ arbitrarily chosen as 1/2. We can determine the duration $\Delta_N$ for the state $|\chi^{(N)}_\pm \rangle$ by summing the above expression for $\langle \cos \theta \rangle (s)$ and expanding the result to second order around its extremum, obtaining

$$\Delta_N \approx \frac{2}{\pi} \sqrt{\frac{1}{\Gamma_N} \left[ 1 - \gamma / \cos \left( \frac{\pi}{N+1} \right) \right]},$$

where $\Gamma_N = \alpha(N+1)^2 - (N+1)$ with $\alpha = 2/3 - 1/\pi^2$. The shape of $\Delta_N$ as a function of $N$ is similar to the dashed curve on the upper panel of Fig. 2, independently of the specific value of $\gamma$. In particular, the decrease of this duration for large $N$ is due to the factor $\Gamma_N$.

Finding a process that drives the system to an optimal state $\chi^{(N)}_\pm$ guarantees an efficient orientation together with a large duration if the dimension $N$ of the subspace $H_N$ generated by the dynamics is relatively low.

[10]. The lower frame of Fig. 2 shows that the HCP-laser combination of appropriate areas leads in a single step to a wave function that is remarkably close to the optimal state $|\chi^{(N)}_-\rangle$ (more than 90% for $1.5 < A_{\text{HCP}} < 5$). Figure 2 also indicates how the dimension $N$ of the embedding subspace can be chosen by the value of $A_{\text{HCP}}$ with $A_L = A_{\text{HCP}}/2.5$. Notice the linear character of this necessarily stepwise function. In the island region of Fig. 1, the dynamics also generates a state close to an optimal one: $|\langle \chi^{(5)}_- | \phi(s_{\text{max}}) \rangle |^2 \approx 0.86$ for $A_{\text{HCP}} = 1.25$ and $A_L = 3.7$. For comparison, we note that the same optimal states are reached in [10] by a different process involving 15 short HCP kicks sent at specific times and with a low amplitude in order to remain in a given subspace.

![FIG. 3: Orientation as a function of dimensionless time for (i) $A_{\text{HCP}} = 3$ and $A_L = 3/2.5$ (solid line) and (ii) the optimal state $\chi^{(5)}_\pm$ with a time translation (dashed line).](image)
keeping $A_L$ fixed, one obtains orientation revivals of the same absolute values but opposite sign. The direction of the orientation can thus be controlled by the sign of the HCP pulse.

FIG. 4: Same as Fig. 1 for the dimensionless temperature $\tilde{T} = 5$.

Considering the effect of temperature amounts to statistically average over the solutions of the Schrödinger equation with different initial conditions $|j, m\rangle$ weighed by a Boltzmann factor. Figure 4 shows the maximal orientation, measured by the appropriate expectation value of $\cos \theta$, as a function of the field parameters for a dimensionless temperature $\tilde{T} = kT/B = 5$ (which corresponds to $T \approx 5$ K for the LiCl molecule). Notice that the island disappears while the region around the straight line $A_L = A_{\text{HCP}}/2.5$ persists. The efficient and long-lived orientation revivals are therefore robust with respect to thermal averaging and to the field parameters. The efficiency is lower than at $T = 0$K for the same field amplitudes, but one can recover the same value by increasing the amplitudes along the straight line.

In conclusion, we have shown that a combination of a half-cycle pulse and a short nonresonant laser pulse of appropriate amplitudes leads to efficient and long-lived revivals of orientation beyond the known saturation. Furthermore, this is achieved in a controllable manner since the desired target state can be chosen in a set of optimal target states defined in Hilbert subspaces of low dimension and be reached with a projection larger than 90% by a single hybrid pulse. As an illustration, the ground state of a KCl molecule with rotational constant $B \approx 0.13$ cm$^{-1}$ ($\tau_{\text{rot}} \approx 128$ ps) and dipole moment $\mu_0 \approx 10.3$ D gives $A_{\text{HCP}} \approx 3$ for a pulse duration of 2 ps and a HCP amplitude of 100 kV/cm. To be on the optimal line of Figs. 1 or 4 requires $A_L \approx 1.2$ which corresponds to a peak intensity $I \approx 10^{11}$ W/cm$^2$ for the laser field. These parameters lead to $\max_\theta |\langle \cos \theta \rangle| \approx 0.85$ an a duration of approximately $1/8^{th}$ of the rotational period for a cold molecule (see Fig. 3), and to $\max_\theta |\langle \cos \theta \rangle| \approx 0.73$ and a duration of approximately $1/20^{th}$ of the rotational period for $T = 5$ K. The interest of hybrid pulses is not limited to molecular orientation but extends to optimization issues of a large class of systems where symmetries need to be broken or selectively addressed (e. g. the control of tunneling). The central element consists in using an external field that plays individually on couplings of different symmetries. In order to drive the dynamics even closer to an optimal target state, standard optimization algorithms can be used for trains of these hybrid pulses (with for instance the delays and/or the relative amplitudes between the kicks, or even a delay between the HCP and laser pulses) and should require only a low number of hybrid pulses since the first step already brings the system very close to the target state.

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