

Reaching optimally oriented molecular states by laser kicks

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(Received 20 September 2003; published 11 March 2004)

We present a strategy for postpulse molecular orientation aiming both at efficiency and maximal duration within a rotational period. We first identify the optimally oriented states which fulfill both requirements. We show that a sequence of half-cycle pulses of moderate intensity can be devised for reaching these target states.

DOI: 10.1103/PhysRevA.69.033402

PACS number(s): 33.80.-b, 32.80.Lg, 42.50.Hz

Molecular orientation plays a crucial role in a wide variety of applications extending from chemical reaction dynamics to surface processing, catalysis, and nanoscale design [1–4]. Static electric field [5] and strong nonresonant long laser pulses [6,7] have been shown to yield adiabatic molecular orientation which disappears when the pulse is off. Noticeable orientation that persists after the end of the pulse (and even under thermal conditions) is of special importance for experiments requiring field-free transient orientation. It has recently been shown that very short pulses combining a frequency ω and its second harmonic 2ω excite a mixture of even and odd rotational levels and have the ability to produce such postpulse orientation [8]. But even more decisive has been the suggestion to use half-cycle pulses (HCPs), that through their highly asymmetrical shape induce a very sudden momentum transfer to the molecule which orients under such a kick after the field is off [9,10]. Both the $(\omega+2\omega)$ and the kick mechanisms have received a confirmation from optimal control schemes [11]. The caveat is that the postpulse orientation is maintained for only short times. Recently, the use of a train of kicks to increase the efficiency of the orientation has been suggested in optimal control strategies [11] and applied to molecular alignment [12] and orientation of a two-dimensional (2D) rotor [13]. However, due to the strength of the kicks used, only the efficiency of the process has been optimized, its duration decreasing strongly. In the present paper, we propose a control strategy using specially designed series of kicks delivered by short HCPs, that allows to significantly enhance the duration of the orientation, maintaining a high efficiency. Our construction is first based on the identification of target states which fulfill the previous requirement. These states are characterized by the fact that they only involve a limited number of the lowest lying rota-

tional levels and that they maximize the orientation efficiency within the corresponding restricted rotational spaces. At a second stage, we show that these selected states can be reached by a train of kicks, acting at appropriately chosen times. The choice of the strength of the pulses (taken equal for simplicity), together with the total number of kicks allow to approach these target states with good accuracy.

The time evolution of the molecule (described in a 3D rigid rotor approximation) interacting with a linearly polarized field is governed by the time-dependent Schrödinger equation (in atomic units)

$$i \frac{\partial}{\partial t} \psi(\theta, \phi, t) = [BL^2 - \mu_0 F(t) \cos \theta] \psi(\theta, \phi, t), \quad (1)$$

where L is the angular momentum operator, B the rotational constant, μ_0 the permanent dipole moment, and $F(t)$ the field amplitude. θ denotes the polar angle between the molecular axis and the polarization direction of the applied field. The motion related to the azimuthal angle ϕ can be separated due to cylindrical symmetry. From now on, we assume a sudden approximation due to the short durations τ of the HCPs, as compared to the molecular rotational period $T_{rot} = \pi/B$. For relatively low l (where l labels the quantum eigenstates of L^2), this amounts to the definition of a dimensionless, small perturbative parameter $\varepsilon = \tau B$. This definition, together with a rescaling of time $s = t/\tau$ (such that $s \in [0, 1]$ during the pulse) leads to an equation suitable for the application of time-dependent unitary perturbation theory [14,15]

$$i \frac{\partial}{\partial s} \psi(\theta, \phi, s) = [\varepsilon L^2 - E(s) \cos \theta] \psi(\theta, \phi, s), \quad (2)$$

where $E(s) = \mu_0 \tau F(\tau s)$. At lowest order in ε , the emerging dynamical picture is the following [15,16]: an individual HCP imparts a kick to the molecule described by an effective instantaneous evolution operator $e^{iA \cos \theta}$, where $A = \int_0^1 E(s) ds$ is the total pulse area. Between two kicks, the

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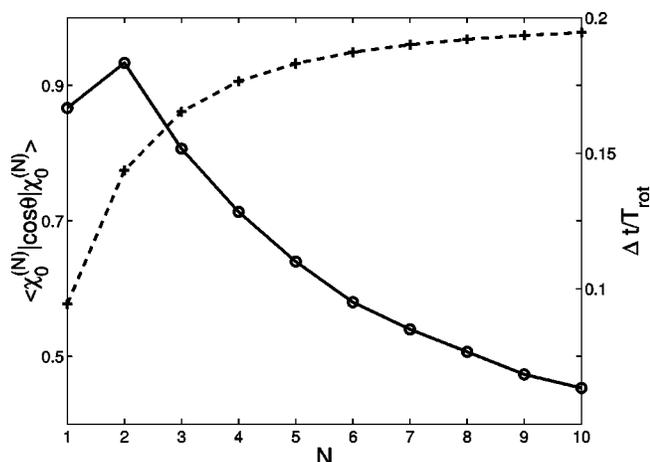


FIG. 1. Maximal orientation efficiency (crosses) and associated duration (open circles) as a function of N , where $N+1$ is the dimension of the rotationally excited subspace $\mathcal{H}_0^{(N)}$ (see text). The solid and dashed lines are just to guide the lecture.

molecule evolves under the effect of its field-free rotation $e^{-i\epsilon L^2 s}$.

The goal of the field driven molecular orientation is to maximize (or to minimize, depending on the choice of the orientation) for the longest time duration, the expectation value $\langle \cos \theta \rangle(s) = \langle \psi(\theta, \phi, s) | \cos \theta | \psi(\theta, \phi, s) \rangle$ after the pulse is over. An understanding of this process can be obtained by analyzing the molecular dynamics in a finite subspace $\mathcal{H}_m^{(N)}$ generated by the first $(N+1)$ eigenstates of L^2 , i.e., $|l, m\rangle$ ($l = |m|, |m|+1, \dots, N+|m|$) for a molecule initially in the state $|l_0 \geq m, m\rangle$. The justification of such a reduction is in relation with the finite amount of energy that a finite number of HCPs of a given area A can transfer to the molecule. The mathematical advantage it offers is the consideration of an operator

$$C_m^{(N)} = P_m^{(N)} \cos \theta P_m^{(N)} \quad (3)$$

($P_m^{(N)}$ being the projector on the subspace $\mathcal{H}_m^{(N)}$ which, as opposed to $\cos \theta$, has a discrete spectrum. It turns out that the state $|\chi_m^{(N)}\rangle$, which maximizes the orientation in the subspace $\mathcal{H}_m^{(N)}$, is the eigenstate of $C_m^{(N)}$ with the highest eigenvalue. Using the approximation $\langle l, m | \cos \theta | l \pm 1, m \rangle \approx 1/2$ valid for $l \gg m$, straightforward algebra leads to

$$|\chi_m^{(N)}\rangle \approx \left(\frac{2}{N+2} \right)^{1/2} \sum_{l=|m|}^{l=|m|+N} \sin\left(\pi \frac{l+1-|m|}{N+2} \right) |l, m\rangle. \quad (4)$$

Since the quantum number m related with the azimuthal angle is conserved, we will not write it explicitly, unless necessary. The maximal orientation in this subspace is found to be

$$\langle \chi_m^{(N)} | \cos \theta | \chi_m^{(N)} \rangle \approx \cos\left(\frac{\pi}{N+2} \right). \quad (5)$$

For a temperature $T=0$ K ($m=0$), Fig. 1 gathers two informa-

tions relevant for the characterization of orientation as a function of N ; namely $\langle \chi^{(N)} | \cos \theta | \chi^{(N)} \rangle$ which is the maximum efficiency [approximately given by Eq. (5) that can ideally be expected for a process that stays confined within the finite subspace $\mathcal{H}^{(N)}$, and $\Delta t / T_{rot}$ which measures the relative duration of the orientation over which $\langle \cos \theta \rangle$ remains larger than 0.5 during the field-free evolution of $|\chi^{(N)}\rangle$. The results, expressed as a fraction of the rotational period T_{rot} , are molecule independent. From Fig. 1, we observe that, in order to keep a duration of the order of (1/10)th of the rotational period (which may amount to durations exceeding 10 ps, for heavy diatomic molecules such as, e.g., NaI), N has to be limited to 5 or 6, which seems rather limiting. But this turns out to be sufficient for very efficient orientation. $N=4$ already allows an orientation efficiency larger than 0.91.

Two basic questions are in order: which set of parameters and which number of kicks have to be chosen to (approximately) remain in the subspace $\mathcal{H}^{(N)}$, and which strategies have to be followed to reach the maximum possible efficiency within this subspace? The first question is in relation with the kick momentum transfer operator $e^{iA \cos \theta}$, which is the only evolution operator (as opposed to the free evolution) that rotationally excites the system and forces it to expand on a larger subspace. We can estimate the loss outside $\mathcal{H}^{(N)}$ assuming a preliminary convergence to $|\chi^{(N)}\rangle$ (as shown by Fig. 2) by looking for the smallness of the norm

$$\|(e^{iA \cos \theta} - P^{(N)} e^{iA \cos \theta} P^{(N)}) |\chi^{(N)}\rangle\|^2 = \eta, \quad (6)$$

which, for small A , amounts to

$$\eta \approx [A\pi]^2 / [2(N+2)^3]. \quad (7)$$

This allows us to establish a relation between A and N for a given loss. $N \approx 4$ is found compatible with an $\eta \approx 0.02$ (not more than 2% of the rotational population leaving the subspace $\mathcal{H}^{(4)}$ as far as A does not exceed 1.

The second question can be answered by adapting the strategy suggested for the orientation of a 2D rotor in Ref. [13], which consists in applying laser pulses each time $\langle \cos \theta \rangle$ reaches its maximum. The following argument shows that, if the dynamics stays within the subspace $\mathcal{H}^{(N)}$, such a strategy precisely converges to an optimal state $|\chi^{(N)}\rangle$. This is done by approximating the operators $\cos \theta$ and $e^{iA \cos \theta}$ by $C^{(N)}$ and $e^{iAC^{(N)}}$, respectively. The interaction with a sudden HCP only alters the slope of $\langle C^{(N)} \rangle(s)$ and not its value as is clear from the following relation:

$$\langle e^{-iAC^{(N)}} C^{(N)} e^{iAC^{(N)}} \rangle = \langle C^{(N)} \rangle. \quad (8)$$

Moreover, if a sudden pulse is applied at a time s_i when $\langle C^{(N)} \rangle(s)$ reaches its maximum $C_i = \langle C^{(N)} \rangle(s_i)$, the slope un-

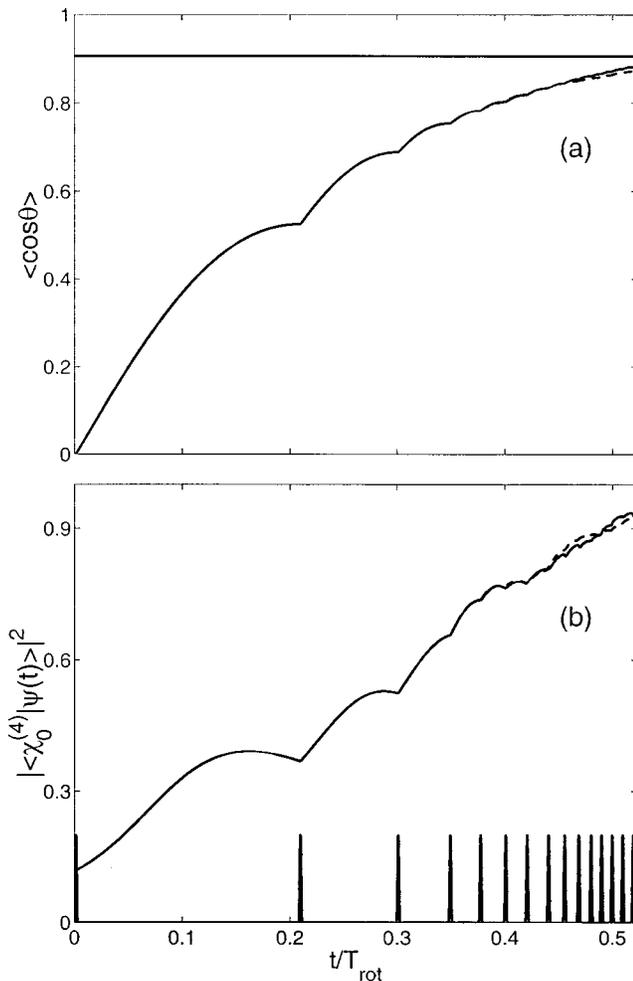


FIG. 2. Orientation dynamics during the train of HCPs at $T = 0$ K: panel (a) for $\langle \psi(s) | \cos \theta | \psi(s) \rangle$ and panel (b) for $|\langle \chi_0^{(4)} | \psi(s) \rangle|^2$. The solid line corresponds to $|\psi(s)\rangle$ calculated exactly and the dashed line to the wave function propagated in the subspace $\mathcal{H}_0^{(4)}$. The train of HCPs is displayed on panel (b) and the optimal orientation is indicated by a horizontal line on panel (a).

dergoes a change from zero to a finite value:

$$\begin{aligned} \frac{d}{ds} \langle C^{(N)} \rangle |_{s_i=0} &= i \langle [\varepsilon L^2, C^{(N)}] \rangle = 0, \\ \frac{d}{ds} \langle C^{(N)} \rangle |_{s_i=0} &= i \langle e^{-iAC^{(N)}} [\varepsilon L^2, C^{(N)}] e^{iAC^{(N)}} \rangle \neq 0. \end{aligned} \quad (9)$$

$\langle C^{(N)} \rangle$ being a periodic, continuously differentiable function, it will reach within the rotational period, a maximum value larger than the one obtained prior to the application of the pulse. Iterating the strategy, we get an increasing but bounded and therefore convergent sequence of C_i 's. Its limit is a fixed point $C_i = C_{i+1}$, corresponding to the eigenvectors of the impulsive propagator $e^{iAC^{(N)}}$ which are also the ones of $C^{(N)}$. Indeed, at a fixed point, the slopes before and after the interaction with the last pulse be zero.

Figure 2 gives two different views of the orientation dynamics under the effect of a train of HCPs, separated by time

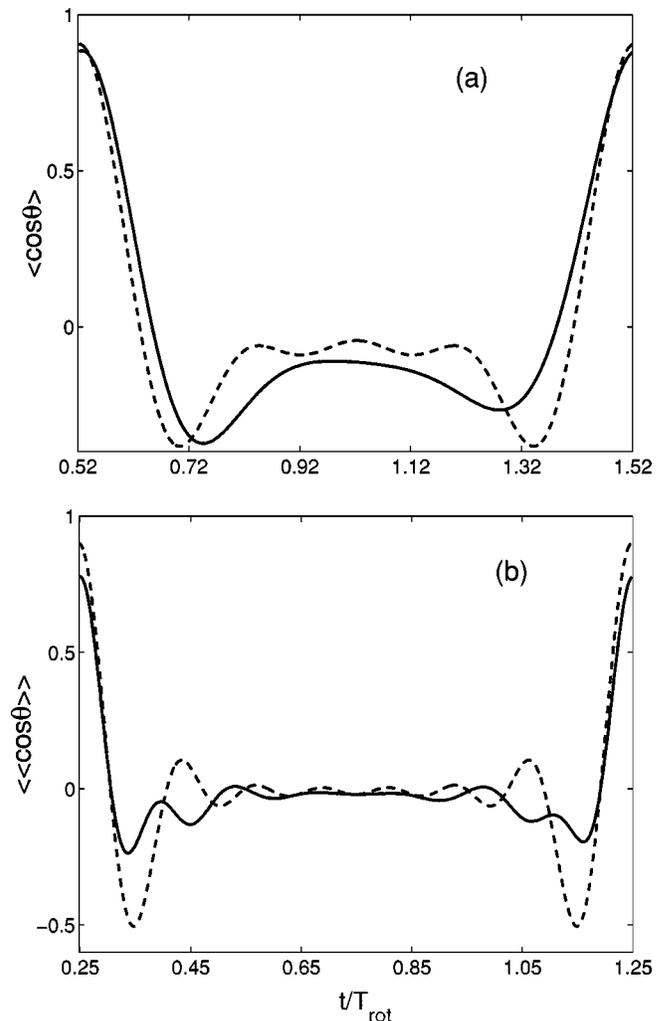


FIG. 3. Postpulse orientation dynamics of the molecule LiCl after interaction with a train of HCPs (the time $t=0$ corresponds to the first kick) in the case $A=1, T=0$ K [panel (a)] and $A=2, T=5$ K [panel (b)]. Solid and dashed lines correspond respectively, to the averages calculated with the exact wave function and the optimal state $|\chi_0^{(4)}\rangle$ on panel (a) and $\rho^{(7)}$ on panel (b)].

delays corresponding to the above discussed strategy of maxima, with identical durations $\varepsilon=0.01$ and pulse areas $A=1$ (that is about 0.3 ps and a field amplitude of 1.5×10^5 V cm $^{-1}$ for LiCl [9]), which leads to a dynamics that remains within the subspace $\mathcal{H}^{(4)}$ for the considered numbers of kicks. From panel (a) it is interesting to note that a single kick produces an orientation of about 0.5, whereas the appropriate application of 15 kicks increases this efficiency up to 0.89, which is almost the optimal limit as found from Fig. 1. On the other hand, the comparison of the average $\langle \cos \theta \rangle$ calculated with the exact wave function $|\psi(s)\rangle$ and with the one propagated in the subspace $\mathcal{H}_0^{(4)}$, are close enough to support the claim that the rotational dynamics actually resides within $\mathcal{H}_0^{(4)}$. Panel (b) shows the way the wave function $|\psi(s)\rangle$ gets close to the optimally oriented state $|\chi_0^{(4)}\rangle$, showing thus the successful outcome of the process. The difference between the two dynamics can be also estimated by Eq. (7). Here again, the close convergence of the two calcula-

tions shows a coherent choice of A , N , and the number of kicks for appropriately describing the dynamics.

The postpulse dynamics, which is our main concern, is displayed on Fig. 3 [panel (a)]. A result expected from the previous analysis, but particularly remarkable with respect to previous proposals, is obtained with an efficiency of about 0.89 and a duration of the order of (2/10)th of the rotational period (that is about 2 ps for a light molecule like LiCl and 20 ps for a heavy one, like NaI).

Orientation is subject to a drastic decrease with temperature [10,11]. This is basically due to the fact that, with non-zero temperature, the initial state is a superposition of a statistical ensemble of rotational states with $m \neq 0$, which tends to misalign the molecule. The efficiency of the orientation is characterized by an additional average of $\langle \cos \theta \rangle$ over the density operators $\rho_m(s)$:

$$\langle \langle \cos \theta \rangle \rangle (s) = \sum_{m \in Z} \text{Tr}[\rho_m(s) \cos \theta]. \quad (10)$$

We recall that $\rho_m(s)$ evolves according to the von Neumann equation

$$\frac{d}{ds} \rho_m(s) = i[\rho_m(s), \varepsilon L^2 - E(s) \cos \theta] \quad (11)$$

with as an initial condition

$$\rho_m(0) = \frac{1}{Z} \sum_{l \geq |m|} |l, m\rangle e^{-Bl(l+1)/kT} \langle l, m|, \quad (12)$$

where $Z = \sum_{m \in Z} \sum_{l \geq |m|} e^{-Bl(l+1)/kT}$ is the partition function and k the Boltzmann constant. Following our previous analysis, we are looking for the optimal density operator which maximizes $\langle \langle \cos \theta \rangle \rangle$ in the subspace $\mathcal{H}^{(N)}$, which is given by $\rho^{(N)} = \sum_m \rho_m^{(N)}$, where $\rho_m^{(N)} = |\chi_m^{(N)}\rangle \text{Tr}[\rho_m^{(N)}] \langle \chi_m^{(N)}|$ with the con-

straint related to the conservation of m , expressed as $\text{Tr}[\rho_m^{(N)}]$ to be kept constant

$$\text{Tr}[\rho_m^{(N)}] = \frac{1}{Z} \sum_{|m|}^{l=|m|+N} e^{-Bl(l+1)/kT}. \quad (13)$$

The effect of a sudden pulse on ρ is $e^{-iA \cos \theta} \rho e^{iA \cos \theta}$, and because its optimal value corresponds to a fixed point of the $\langle \langle C^{(N)} \rangle \rangle (s_i)$ sequence, it is precisely the application of a train of HCPs with individual pulses at times s_i where $\langle \langle \cos \theta \rangle \rangle (s_i)$ reaches its maximum, that converges to the best possible orientation within this model. The resulting dynamics is plotted in Fig. 3 [panel (b)], with a maximum efficiency of about 0.75 and a duration of about (1/20)th of the rotational period. To our knowledge, this is the largest duration and efficiency achieved up to date for a thermal ensemble.

In conclusion, we have presented tools for controlling molecular orientation dynamics using a train of HCPs, achieving both efficiency and duration of the postpulse orientation. Moreover, this scheme can be expected to be transposable to a generic system, with free periodic dynamics governed by a Hamiltonian H_0 , and for which we are aiming to optimally control an observable \mathcal{O} (i.e., maximize or minimize the average $\langle \mathcal{O} \rangle (t)$ of an upper or lower bounded operator \mathcal{O} which does not commute with H_0). This could be done through a device that perturbs the system according to a unitary operator U , which commutes with \mathcal{O} , such that its application does not alter $\langle \mathcal{O} \rangle = \langle U^{-1} \mathcal{O} U \rangle$ on one hand, and the optimal target state is an eigenfunction of both \mathcal{O} and U on the other hand. This optimum corresponds to a fixed point of the sequence $\mathcal{O}_i = \langle \mathcal{O} \rangle (t_i)$, where t_i are the times when $\langle \mathcal{O} \rangle (t)$ reaches its maximum (or minimum) under the free evolution. In particular, this scheme provides a comprehension of previous works on alignment and orientation of 2D and 3D rotors [12,13].

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- [1] P. R. Brooks, *Science* **193**, 11 (1976).
 [2] F. J. Aoiz, *Chem. Phys. Lett.* **289**, 132 (1998).
 [3] T. Seideman, *Phys. Rev. A* **56**, R17 (1997).
 [4] H. Stapelfeldt and T. Seideman, *Rev. Mod. Phys.* **75**, 543 (2003).
 [5] L. Cai, J. Marango, and B. Friedrich, *Phys. Rev. Lett.* **86**, 775 (2001).
 [6] M. J. J. Vrakking and S. Stolte, *Chem. Phys. Lett.* **271**, 209 (1997).
 [7] S. Guérin, L. P. Yatsenko, H. R. Jauslin, O. Faucher, and B. Lavorel, *Phys. Rev. Lett.* **88**, 233601 (2002).
 [8] C. M. Dion, A. D. Bandrauk, O. Atabek, A. Keller, H. Umeda, and Y. Fujimura, *Chem. Phys. Lett.* **302**, 215 (1999).
 [9] C. M. Dion, A. Keller, and O. Atabek, *Eur. Phys. J. D* **14**, 249 (2001).
 [10] M. Machholm and N. E. Henriksen, *Phys. Rev. Lett.* **87**, 193001 (2001).
 [11] C. M. Dion, A. Ben Haj Yedder, E. Cancès, A. Keller, C. L. Bris, and O. Atabek, *Phys. Rev. A* **65**, 063408 (2002).
 [12] M. Leibscher, I. S. Averbukh, and H. Rabitz, *Phys. Rev. Lett.* **90**, 213001 (2003).
 [13] I. S. Averbukh and R. Arvieu, *Phys. Rev. Lett.* **87**, 163601 (2001).
 [14] D. Daems, A. Keller, S. Guérin, H. R. Jauslin, and O. Atabek, *Phys. Rev. A* **67**, 052505 (2003).
 [15] D. Sugny, A. Keller, O. Atabek, D. Daems, S. Guérin, and H. R. Jauslin, *Phys. Rev. A* (to be published).
 [16] N. E. Henriksen, *Chem. Phys. Lett.* **312**, 196 (1999).