

Molecular Alignment by Trains of Short Laser Pulses

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We show that a dramatic field-free molecular alignment can be achieved after exciting molecules with proper trains of strong ultrashort laser pulses. Optimal two- and three-pulse excitation schemes are defined, providing an efficient and robust molecular alignment. This opens new prospects for various applications requiring macroscopic ensembles of highly aligned molecules.

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Molecular alignment and orientation play an important role in chemical reaction dynamics, surface processing, and ultrafast optics. Strong nonresonant laser fields have been shown to yield molecular alignment along the field polarization direction [1–4] by creating pendular molecular states [5–7]. However, the adiabatic molecular alignment produced by a relatively long pulse disappears when the pulse is off. On the other hand, very short pulses (100 fs and less) excite rotational wave packets that yield a noticeable aligned shape *after the end of the pulse* [8–13], even under thermal conditions [14]. Initial experiments have been performed showing the alignment of macroscopic samples of I_2 molecules with a single short laser pulse [15]. This is of special importance for applications that require transient molecular alignment at *field-free conditions*. Generation of ultrashort laser pulses [16,17] and control of high harmonic generation [18] are only a few potential applications to mention. The ability to (transiently) align molecules to the highest possible degree is crucial for applications of this kind.

As we show in the present work, there is a limit to the degree of alignment that can be attained with a single intense ultrashort laser pulse. In order to achieve an enhanced field-free molecular alignment beyond this limit, more complex pulse shapes should be used. Methods of optimal control have been applied to this problem in the past, providing rather sophisticated field patterns [19–21]. Recently, a novel strategy for producing angularly squeezed states of a rigid rotor by a specially designed series of short laser pulses was suggested [22]. The proposed "accumulative squeezing" scheme leads to a dramatic narrowing of the rotor angular distribution upon increasing the number of the pulses. An atom optics realization of this strategy [23] has been experimentally demonstrated [24]. Enhanced molecular alignment by trains of ultrashort laser pulses seems to be a feasible experimental procedure as well.

The present work provides the guidelines and defines conditions for a forthcoming experiment of this kind. We consider the simplest excitation schemes involving only a small number of short pulses, which can be easily realized experimentally even without pulse shaping. The

limited number of pulses allows for a complete optimization of the related excitation parameters and provides even better and more robust alignment compared to the accumulative squeezing approach [22–24].

The Hamiltonian of a driven 3D rigid rotor (linear molecule) is

$$H = \frac{\vec{L}^2}{2I} + V(\theta, t), \quad (1)$$

where L is the angular momentum of the rotor, and I is its moment of inertia. A linear molecule without a permanent dipole couples with the external field via induced polarization. For nonresonant laser fields, this interaction, averaged over the fast optical oscillations, is

$$V(\theta, t) = -\frac{1}{4}\mathcal{E}^2(t)[(\alpha_{\parallel} - \alpha_{\perp})\cos^2(\theta) + \alpha_{\perp}]. \quad (2)$$

Here, α_{\parallel} and α_{\perp} are the components of the polarizability, parallel and perpendicular to the molecular axis, respectively, and $\mathcal{E}(t)$ is the envelope of the laser pulse. If the interaction with the laser field is much shorter than the dominant periods within the excited rotational wave packet, the motion of the wave packet is "frozen" during the interaction and the wave function immediately after the pulse (applied at $t=0$) is $\psi(\theta, 0^+) = \exp(iP\cos^2\theta)\psi(\theta, 0)$. Here, the dimensionless pulse strength $P = (\alpha_{\parallel} - \alpha_{\perp})I \int dt \mathcal{E}^2(t)/(4\hbar^2)$ has been introduced. If we assume that the rotor is initially in its ground state $\psi(\theta, 0) = Y_0^0(\theta)$, the wave function at time τ after the pulse is

$$\psi(\theta, \tau) = \frac{1}{\sqrt{4\pi}} \sum_{l=0}^{\infty} c_l \exp[-il(2l+1)\tau] Y_{2l}^0(\theta), \quad (3)$$

where $\tau = t\hbar/I$ is the dimensionless time. The coefficients c_l are given by

$$c_l = \sqrt{\pi(4l+1)}(iP)^l \times \frac{\Gamma(l+\frac{1}{2})}{\Gamma(2l+\frac{3}{2})} {}_1F_1\left[l+\frac{1}{2}, 2l+\frac{3}{2}, iP\right], \quad (4)$$

where ${}_1F_1$ is the confluent hypergeometric function. The

coefficients in Eq. (4) are obtained by expanding $\exp(iP\cos^2\theta)$ in terms of spherical harmonics. The extremely rich space-time dynamics of the wave function in Eq. (3), including angular focusing, followed by a number of semiclassical catastrophes is discussed in detail elsewhere [25]. We stress here that the wave function shows periodic behavior in time with a revival period of $T_{\text{rev}} = 2\pi$.

The degree of molecular alignment can be quantitatively characterized by the alignment factor $A(\tau) = \langle 1 - \cos^2\theta \rangle$. The alignment factor defined this way coincides with the variance in θ for well-aligned molecules. It tends to zero when the alignment turns perfect, and shows a nice scaling with the number of pulses in the accumulative squeezing approach [22]. Using Eq. (3) we obtain

$$A(\tau) = 1 - M - \frac{1}{2\pi} \text{Re} \sum_{l=0}^{\infty} c_l c_{l+1}^* \exp[i(4l+3)\tau] \times \frac{(2l+1)(2l+2)}{4l+3} \frac{1}{\sqrt{(4l+1)(4l+5)}}, \quad (5)$$

with

$$M = \frac{1}{4\pi} \sum_{l=0}^{\infty} |c_l|^2 \frac{1}{4l+1} \left[\frac{(2l+1)^2}{4l+3} + \frac{4l^2}{4l-1} \right]. \quad (6)$$

Here, M is the time-averaged value of $\langle \cos^2\theta \rangle$. Figure 1 shows the quantum mechanical alignment factor (solid line) of a 3D rotor kicked by a short pulse at $\tau = 0$. For a strong enough kick, the initial stage of the time evolution can be explained in classical terms (for a 2D rotor see [22,23]). For this purpose, consider an isotropic ensemble of classical rotors (or, equivalently, an ensemble of particles freely moving on a sphere) subject to a kick. A motionless classical particle initially at angle θ_0 , gains the angular velocity $\omega = -P \sin(2\theta_0)$ as a result of a pulsed interaction given by Eq. (2). The classical alignment factor may be calculated as

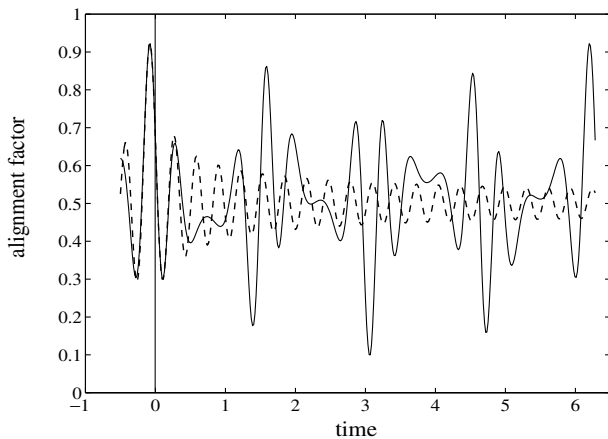


FIG. 1. Quantum mechanical (solid line) and classical (dashed line) alignment factor for kick strength $P = 10$.

$$A_{\text{cl}}(\tau) = 1 - \frac{1}{2} \int_0^\pi d\theta_0 \sin\theta_0 \cos^2[\theta_0 - P\tau \sin(2\theta_0)] = \frac{1}{2} + \frac{1}{6} {}_1F_2 \left[1; \frac{7}{4}, \frac{5}{4}; -(P\tau)^2 \right] - \frac{8}{15} \tau {}_1F_2 \left[2; \frac{7}{4}, \frac{9}{4}; -(P\tau)^2 \right]. \quad (7)$$

This result is shown for comparison by the dashed line in Fig. 1. $A_{\text{cl}}(\tau)$ reaches a minimum of $A_{\text{min}} \approx 0.30$ at $P\tau \approx 1.1$ and then approaches the asymptotic value $A(\tau \rightarrow \infty) = 1/2$ in an oscillatory way. For $\tau \ll 1$, the quantum mechanical alignment factor coincides with the classical result. In later stages of the evolution, full and fractional revivals [26] lead to relocalization of the rotational wave packets at $T_{\text{rev}}/4 = \pi/2$ and $T_{\text{rev}}/2 = \pi$. Surprisingly, the degree of alignment during the fractional revivals is considerably larger than at the initial, classical-like, stage of evolution. The alignment factor reaches the global minimum at $\tau \approx \pi$, which is 3 times smaller than the initial, classical minimum. The appearance of an extremely narrow angular state at half of the revival period has been numerically observed in several studies (see, e.g., [14,16]), but, to the best of our knowledge, it has been never explained, and no estimates have been given to the lower limit of the alignment factor in this time domain. We further note that the appearance of a global minimum of the quantum mechanical alignment factor at $\tau \approx \pi$ is a truly three-dimensional effect, and it does not show up in the alignment of a 2D rotor [22,23].

We show here that despite the quantum nature of the phenomenon, this global minimum can be related to the classical dynamics analytically continued to *negative times*. Indeed, as can be seen in Fig. 1, the classical alignment factor has a pronounced maximum $A_{\text{max}} \approx 0.925$ at $P\tau \approx -0.8$. The increase of the alignment factor can be interpreted as a focusing of the particles around $\theta = \pi/2$ in the equatorial plane when propagating back in time after a kick. The periodicity of the quantum mechanical alignment factor allows us to relate its value in the $\tau \approx \pi$ region to the corresponding values in the classical domain ($\tau \ll 1$). It follows from Eq. (5) that $A(\pi + \tau) = 1 - A(\tau) + (1 - 2M)$ where M is given by Eq. (6). For a sufficiently large kick strength, M tends to the classical time-averaged value of $\langle \cos^2\theta \rangle = 1/2$. Therefore, $A(\pi + \tau) \approx 1 - A_{\text{cl}}(\tau)$, and the minimal alignment factor achievable by a single strong pulse is $A_{\text{min}} \approx 1 - A_{\text{max}} \approx 0.075$. This asymptotic value can be approached by increasing the kick strength. However, the dependence of the global minimum near $\tau \approx \pi$ on P is nonmonotonic. As can be seen in Fig. 2 (solid line), there are "magic" kick strengths that provide local minima of the alignment factor as the function of P ($P_m = 5.4, 11.8, 18.2, \dots$).

In order to align molecules beyond the limit of $A_{\text{min}} = 0.075$, a single pulse is not sufficient. However, the degree of alignment can be considerably improved by applying a

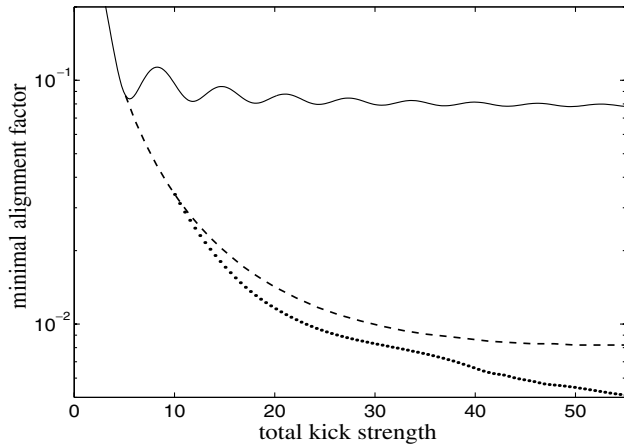


FIG. 2. Optimal alignment factor of a 3D rotor kicked with a single pulse (solid line), or with a sequence of two (dashed line) or three (dotted line) pulses for the given total kick strength P_t .

second pulse around the time of minimal angular spread [22]. This leads to a simple, but effective two-pulse alignment scheme. The first pulse prealigns the molecules in the harmonic region of the angular interaction potential while the second pulse completes the angular focusing. For better focusing, the second pulse should be much stronger than the first one, so that the kinetic energy gained by the molecules during the first kick can be neglected. In the classical limit, such a strong second pulse provides a complete alignment of the "frozen" angular distribution formed by the first pulse. In order to estimate the efficiency of the process, we choose the first "magic" kick strength $P_m = 5.4$ for the first pulse. If the strength of the second kick is $P_2 \geq 50$, the minimal alignment factor reaches $A_{\min} = 0.017$, which is more than 4 times better compared to the single-pulse case.

In order to explore the prospects of multipulse alignment, we make use of optimal control theory. For the experimentally interesting case of a small number of pulses, the optimal control [27] reduces to the optimization problem with few parameters. We minimized the quantum alignment factor with respect to the kick strengths P_1, \dots, P_N , delay times $\tau_1, \dots, \tau_{N-1}$ between pulses, and the detection time τ_d after the last pulse. As a constraint, the total kick strength $P_t = \sum_{i=1}^N P_i$ was kept constant, and we studied the dependence of the optimal solution on this parameter as well. The results of the optimization are shown in Fig. 2. Here, the minimal alignment factor for $N = 1$ (solid line), $N = 2$ (dashed line) and $N = 3$ (dotted line) pulses is plotted as a function of P_t . Table I shows exemplary excitation parameters. For $P_t \leq 5$, the single-pulse excitation is optimal. The optimal solution shows a bifurcation (branching) at $P_t \approx 5.0$, after which a considerable improvement of the alignment can be provided by splitting the available laser energy into two pulses. For angular squeezing with two

TABLE I. Optimal sequence of pulses for a given number of kicks (no.) with total kick strength P_t . Shown are the kick strengths P_1, P_2, P_3 , the delay times between the kicks (τ_1 and τ_2), the detection time τ_d , and the minimal alignment factor A_{\min} .

No.	P_t	P_1	P_2	P_3	τ_1	τ_2	τ_d	A_{\min}
1	5	5	2.98	0.088
2	10	4.56	5.65	...	2.88	...	0.06	0.034
2	55	4.60	50.4	...	2.94	...	0.01	0.008
3	60	4.38	2.88	52.7	2.86	0.13	0.01	0.005

pulses, the optimal solution is very similar to the previously described heuristic double-pulse scheme. With optimized parameters (see Table I), the minimal alignment factor is $A_{\min} = 0.008$. Our simulations show that the double-pulse quantum alignment factor saturates at this level already for $P_t \approx 50$. However, the optimal solution experiences another branching even before that. At $P_t \approx 11$ a three-pulse solution emerges providing better alignment for the same total kick strength (see Table I). Again, the first two pulses create a well prelocalized quantum state that is further squeezed in angle by the third pulse acting as a strong "classical" kick. The three-pulse alignment improves with increasing the total kick strength and saturates at $A \approx 0.005$ for $P_t \approx 60$.

The above optimized trains of laser pulses not only provide the best possible alignment, but also offer the solution that is least sensitive to the fluctuations of the control parameters (because of the stationary character of the optimal solution). We show this reduction of noise sensitivity in Fig. 3. The figure displays the minimal alignment factor resulting from two short pulses applied to a rotor in the ground state as a function of the delay time τ_1 between them. The optimal solution achievable

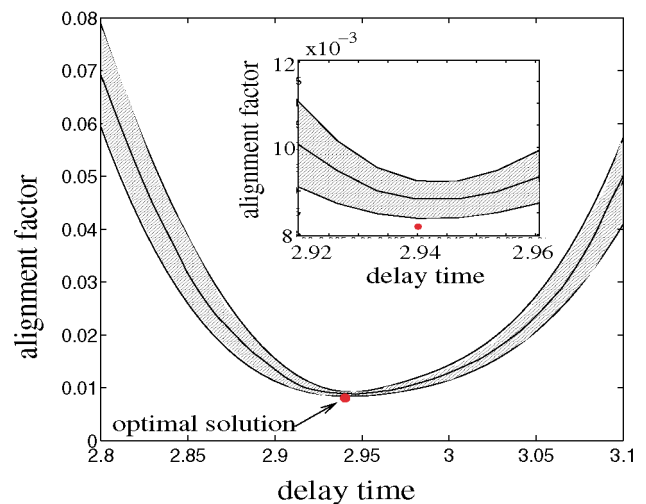


FIG. 3 (color online). Noise reduction near the optimal solution.

with the total kick strength $P_t \approx 55$ (see Table I) is indicated by a dot. We scanned the delay time τ_1 while keeping the kick strengths and the detection time fixed. For every τ_1 , Gaussian jitter with the half-width $\Delta\tau_1 = 0.02$ was added to the delay time. The variance of the resulting alignment factor is shown by the gray band in Fig. 3, while the middle line represents the average alignment factor. A considerable reduction of the influence of the noise can be seen close to the optimal point where the alignment factor takes its minimal value.

As an example, we consider laser alignment of iodine monochloride that has polarizability anisotropy $\alpha_{\parallel} - \alpha_{\perp} = 9 \text{ \AA}^3$, and rotational constant $B = 0.1142 \text{ cm}^{-1}$ corresponding to the period of $\tau_r = 1/(2Bc) \approx 146 \text{ ps}$. We assume that the envelope of the laser pulse $\mathcal{E}^2(t) = 4\pi g(t)I_p/c$ (where I_p is peak intensity) has a Gaussian shape $g(t) = \exp(-t^2/\sigma^2)$. For a pulse duration of $\sigma = 100 \text{ fs}$, the double-pulse solution shown in Table I with $A_{\min} = 0.034$ can be realized with the intensities $I_{p1} = 2.88 \times 10^{12} \text{ W/cm}^2$ and $I_{p2} = 3.42 \times 10^{12} \text{ W/cm}^2$.

In summary, we have demonstrated that optimal trains of short nonresonant laser pulses can lead to a sizable field-free molecular alignment. A sequence of several properly timed and energy balanced pulses of *moderate intensity* may temporarily squeeze the molecular angular distribution well beyond the limits of a brute-force excitation by a single strong pulse. The simplicity of the field forms involved allows for efficient optimization for the best alignment with the least sensitivity to the control parameter fluctuations. Even in this simple case, the optimal solution demonstrates a nontrivial character, with multiple local minima and branching phenomena. The optimized pulse trains derived here in the impulsive approximation may also serve as initial guesses for more sophisticated closed loop learning control approaches [28,29] to laser molecular alignment. The multiple-pulse angular squeezing provides a regular way for creating macroscopic samples of highly aligned molecules needed for various applications [16–18].

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