

Conservation of Molecular Alignment for Cyclic Rotational Wave Packets in Periodic Pulse Trains

Juan Ortigoso

Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006, Madrid, Spain

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The existence of states for which molecular alignment can be maintained for long periods of time is shown. These states, consisting of coherent superpositions of rotational states, are found among cyclic states of the generalized Floquet operator corresponding to a molecule in a short nonresonant laser pulse. For a single pulse alignment can be maintained, in some cases, for more than 40 times the pulse duration. Because of the special properties of these coherent states, arbitrarily long alignment can be achieved by using well-timed pulse trains.

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In the recent past there has been an increasing interest in the theoretical and experimental study of molecular orientation and alignment (for a review, see [1]). Among the many techniques proposed so far the most promising are those based on the interaction between a pulsed nonresonant laser field and molecular polarizability. These techniques can produce field-free alignment, as the molecules may end up, after the pulse is over and for nonadiabatic interactions, in a coherent superposition of rotational states. These superpositions give rise to further recurrences in the alignment [2]. Leibscher *et al.* [3] have shown that there is a limit for the degree of alignment that can be obtained with a single laser pulse. These authors have used optimal control theory to design laser fields which allow to overcome this limit, and showed that optimized trains of laser pulses provide robust alignment. A related scheme [4] suggests that narrow angular distributions can be achieved by increasing the number of tailored short pulses. Orientation is more difficult to obtain than alignment, since a symmetry-breaking mechanism is required. Dion *et al.* [5] have tailored laser pulses that optimize orientation by using genetic algorithms. They also suggested that trains of kicks can enhance orientation. In the present Letter I show the existence of rotational wave packets that, when subject to a single short nonresonant laser pulse retain a large degree of alignment up to more than 40 times the pulse duration. Because of the special characteristics of these states the alignment can be maintained as long as desired by using a sequence of identical pulses.

The localization properties of wave packets are usually destroyed during their time evolution. An initial quasi-classical evolution is rapidly followed by collapses and revivals [6]. However, it is well known for several time-periodic systems as, for example, Rydberg states of atoms in polarized microwave fields, that nondispersive wave packets exist [7], and are given by *localized* Floquet eigenstates. As stated by Buchleitner *et al.* [6], the existence of such wave packets is not obvious due to the

complexity of the Floquet spectrum. The discovery of nonspreading wave packets for atoms subject to periodic external perturbations has been based in the investigation of the corresponding classical analog. Also, it has been suggested that nonspreading states can exist for diatomic molecules with permanent dipole moment in circularly polarized electric fields [8]. Kim *et al.* gave an approximate expression for these wave packets and discussed a method for its generation and control.

A rotating molecule subject to a linearly polarized laser pulse is a nonperiodic system. Aligned states are given by rotational wave packets strongly localized at $\theta \approx 0$ and $\theta \approx \pi$, where θ is the polar angle between the direction of the electric field and the molecular axis. If nondispersive wave packets exist for a nonperiodic system they must be localized eigenstates of the Schrödinger operator $S(t) = H(t) - i\hbar\partial/\partial t$ [9], as explained below. Thus, it is natural to ask if some laser pulse can give rise to states for which the alignment is well conserved during the pulse duration.

Shirley [10], by using Floquet theory, showed how to describe the time-dependent interaction of a two-level quantum system with a periodic electromagnetic field as a time-independent problem. Sambe [11] introduced, for time-periodic systems, the use of a Floquet operator in an extended Hilbert space in which time is treated as another spatial coordinate. This space is formed by the composition of the Hilbert space corresponding to the spatial zeroth-order Hamiltonian and the space formed by all possible periodic functions of time with finite norm. Seleznyova [9] showed that for a quantum mechanical system under a nonadiabatic external perturbation in a time interval $[0, T]$ all the cyclic states of the system, i.e., those for which $\psi(T) = e^{(i\delta)}\psi(0)$, are determined by the eigenvalues (ϵ) and eigenvectors (ϕ_ϵ) of the Schrödinger operator $S(t)$ acting in the extended Hilbert space. Also, she established a connection between the cyclic states of a system in $[0, T]$ and the quasienergy states of a T -periodic system related to it. Thus, a cyclic state for an arbitrary

system, for which not necessarily $H(0) = H(T)$ (which suggests the possibility of extending the present study to nonsymmetric laser pulses), can be written [9] as $|\psi(t)\rangle = \exp(-i\epsilon t/\hbar)|\phi_\epsilon(t)\rangle$, where $\epsilon = -\delta\hbar/T$ and $\phi_\epsilon(T) = \phi_\epsilon(0)$.

The (t, t') method of Peskin and Moiseyev [12] also considers time as an extra coordinate, t' . The solution of the time-dependent Schrödinger equation can be formally written as

$$\tilde{\psi}(x, t) = \psi(x, t', t)|_{t'=t}, \quad (1)$$

where

$$\psi(x, t', t) = \exp[(-i/\hbar)S(t')(t - t_0)]\psi(x, t', t_0). \quad (2)$$

Solutions to the time-dependent Schrödinger equation can be obtained, in this formalism, by using methods developed for time-independent problems, since the Schrödinger operator $S(t')$ is time independent. Peskin and Moiseyev assumed box normalization for t' ($0 \leq t' \leq T$) and also explained how to use periodic boundary conditions by artificially introducing periodicity in a parameter of the Hamiltonian. In the case of a molecule interacting with a single pulse, this is equivalent to consider that the pulse is repeated periodically with period T , which is fully justified for high-frequency lasers. In the (t, t') formalism a generic wave function can be written as an expansion in the basis set of generalized Floquet eigenstates. The time dependence of the wave function is encoded in phase terms and in the basis functions as well. Thus, a wave function that obeys $S(t)\psi(t) = 0$, can be expanded as [9,13]

$$|\psi(t)\rangle = \sum_J \exp[-i\epsilon_J(t - t_0)/\hbar]|\phi_{\epsilon_J}(t)\rangle \langle\langle\phi_{\epsilon_J}|\psi\rangle\rangle, \quad (3)$$

where $\langle\langle\phi_{\epsilon_J}|\psi\rangle\rangle$ is the inner product in the extended Hilbert space. By taking advantage of the periodicity of the eigenvalues and eigenvectors of $S(t)$ the expansion can be limited to the Floquet states that belong to the first Brillouin zone ($\epsilon_{J'} \in [-\pi/T, \pi/T]$) [9,13]:

$$|\psi(t)\rangle = \sum_{J'} \exp[-i\epsilon_{J'}(t - t_0)/\hbar]|\phi_{\epsilon_{J'}}(t)\rangle \langle\phi_{\epsilon_{J'}}(t_0)|\psi(t_0)\rangle, \quad (4)$$

where the inner product has been taken in the Hilbert space of the zeroth-order spatial Hamiltonian.

The Hamiltonian for a linear molecule in a high-frequency nonresonant linearly polarized laser field for an isolated vibronic state, after averaging the square of the electric field over the period of the pulse, is [2]

$$H(t) = B\mathbf{J}^2 - \frac{1}{4}E_0^2g(t)[(\alpha - \alpha_\perp)\cos^2\theta + \alpha_\perp], \quad (5)$$

where B is the rotational constant, \mathbf{J} is the angular momentum operator, α_\parallel and α_\perp are the components of the static polarizability, parallel and perpendicular to the

molecular axis, and E_0 is the strength of the electric field. The time profile, $g(t)$, can be chosen to be a Gaussian centered at $t = 0$, $\exp(-t^2/\sigma^2)$, characterized by a full-width at half maximum $\tau \cong (5/3)\sigma$ (the pulse duration). The eigenstates (cyclic states) of the Schrödinger operator in dimensionless form, $\hat{S}(t') = H(t')/B - (i\hbar/B)\partial/\partial t'$, can be expanded in a basis set of field-free rotational eigenstates $|J, M\rangle$ (M is the projection of \mathbf{J} along the direction of the external field) times a Fourier basis set for the time coordinate $|n\rangle = (1/\sqrt{T}) \times \exp(2\pi i n t'/T)$, where T is the period chosen for the external field. The eigenstates of $\hat{S}(t')$ depend on dimensionless interaction parameters $\omega_\parallel = E_0^2\alpha/(4B)$ and $\omega_\perp = E_0^2\alpha_\perp/(4B)$. Because of the dimensionless form of $\hat{S}(t')$, \hbar/B is a reduced unit of time and B/\hbar is a reduced unit of frequency [2].

The matrix elements needed to build a matrix representation of $\hat{S}(t')$ (valid for $T \gg \sigma$) are

$$\langle n | \exp(-t^2/\sigma^2) | n' \rangle = \frac{\sigma\sqrt{\pi}}{T} \exp\left[\frac{-\pi^2\sigma^2(n' - n)^2}{T^2}\right], \quad (6)$$

and

$$\langle n | -i\frac{\partial}{\partial t} | n' \rangle = \frac{2\pi n'}{T} \delta_{nn'}. \quad (7)$$

When the initial wave function, $|\lambda(t = t_0)\rangle$, is a cyclic state only one generalized Floquet state contributes to the summation in Eq. (4) since $\langle\phi_{\epsilon_j}(t)|\phi_{\epsilon_{j'}}(t)\rangle = \delta_{jj'}$ for any $t \in [0, T]$.

A rotational wave packet given by the projection onto the spatial Hilbert space of a cyclic state at t_0 , $|\lambda\rangle = \sum_{J,n} c_{Jn} |J\rangle |n\rangle$, evolves at time T to

$$U(T, t_0)|\lambda(t_0)\rangle = \exp[-i\epsilon_\lambda(T - t_0)B/\hbar] \sum_J c'_J(t_0) |J\rangle, \quad (8)$$

where $c'_J(t_0) = \sum_n c_{Jn} \exp(2\pi i n t_0)$, and ϵ_λ is the eigenvalue corresponding to $|\lambda\rangle$. Therefore, *global* quasiadiabatic behavior can be obtained for processes that locally are highly nonadiabatic. Adiabatic behavior is usually spoiled if the system traverses, during its time evolution, avoided crossings between eigenstates of the instantaneous Hamiltonian [14].

Selected cyclic states that give rise to large alignment can be created by using tailored microwave pulses that guide the molecule from a field-free eigenstate. Judson *et al.* [15] discussed how to design microwave pulses to create superpositions of rotational eigenstates with a high degree of orientation for diatomic molecules. The characteristics of pulses capable of creating coherent states for asymmetric-top molecules were studied in [16]. Other feasible ways to create these rotational wave

packets should be investigated as, for example, ultrafast pulse shaping in the weak-field regime [17]. If the preparation step fails to produce the selected state the system will end up in a superposition of cyclic states with unknown alignment properties. However, Seleznyova [9] showed that for specific values of T some linear combinations remain cyclic.

The initial alignment can change during the pulse but it is recovered at time T , because the wave packet evolves, at the end of each pulse, to the initial state multiplied by a phase. However, the time evolution of the field-free eigenstates that compose the initial wave function is highly nonadiabatic both locally and globally for pulses with $\sigma \leq \hbar/B$ [2]. This behavior is illustrated in Fig. 1, which shows the time evolution for a molecule in an electric field composed by a sequence of three identical pulses. The time evolution was calculated using the quasienergy states resulting of diagonalizing the (t, t') Hamiltonian matrix. The basis set was formed by 16 field-free rotational eigenstates (J from zero to 30) and 161 Fourier time basis set ($n = -80, \dots, 80$), which amounts to a modest matrix of 2576×2576 . The initial alignment is recovered at the end of each pulse for the cyclic state shown in Fig. 1 (corresponding to the eigenvalue $\epsilon = 23.92$). On the other hand, the evolution is strongly nonadiabatic for initial wave functions corresponding to field-free rotational eigenstates. At the end of the second pulse maximum alignment corresponds to $|J=0\rangle$, but after the third pulse it corresponds to $|J=4\rangle$. This behavior illustrates an interesting situation in which the individual field-free eigenstates that compose a given cyclic state

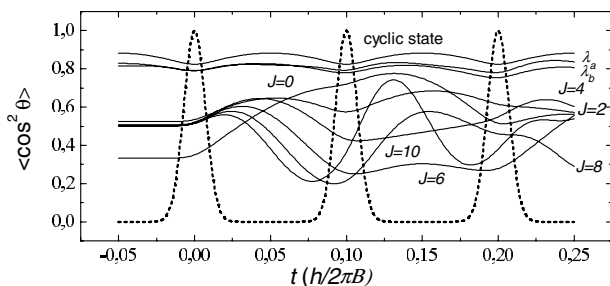


FIG. 1. Alignment $\langle \cos^2 \theta \rangle$, for a cyclic state and six eigenstates of the rotational Hamiltonian, as a function of time (in dimensionless units). The electric field, represented in arbitrary units by the dotted line, is given by a sequence of three identical Gaussian pulses. For each pulse $\sigma = 0.01$, $T = 0.1$, $\omega_{\parallel} = 300$, and $\omega_{\perp} = 0$. The initial cyclic state, at time $t = -0.05$, is given in terms of $|J\rangle$ states by $\lambda(t_0) \approx 0.51|0\rangle + 0.74|2\rangle + 0.38|4\rangle + 0.17|6\rangle + 0.11|8\rangle$. Also the time evolution is shown for initial states corresponding to eigenstates of Floquet operators with $T = 0.11$ [$\lambda_a(t_0) \approx 0.48|0\rangle + 0.71|2\rangle + 0.31|4\rangle + 0.18|6\rangle + 0.21|8\rangle - 0.13|10\rangle - 0.19|14\rangle - 0.15|18\rangle$] and $T = 0.12$ [$\lambda_b(t_0) \approx 0.51|0\rangle + 0.62|2\rangle + 0.57|4\rangle - 0.16|8\rangle$]. Only $|J\rangle$ basis functions with coefficients greater than 0.1 (in absolute value) are given.

evolve in a nonadiabatic fashion but the composite state evolves quasiadiabatically. Figure 1 also shows the time evolution of the alignment for initial states given by cyclic states of Floquet operators with slightly different T values. These states are not eigenstates of the Floquet operator corresponding to the system with $T = 0.1$ and therefore are noncyclic states for it. However, their time evolution illustrates the robustness of the method as large alignment is maintained for these contaminated states. Therefore, it is expected that slight deviations from the ideal case in the preparation step will still give rise to states with sustained alignment.

Only some cyclic states will give rise to sustained alignment during a pulse. Figure 2 shows alignment for pulses with different σ and ω_{\parallel} values. In all cases the period taken was $T = 10\sigma$. For laser pulses with $\sigma \ll \hbar/B$ the degree of misalignment during each pulse of the pulse train is very small as shown in the left panel of Fig. 2. This figure shows the evolution of the alignment under a sequence of three identical pulses with $\sigma = 0.005$. For a molecule with $B = 1 \text{ cm}^{-1}$ this corresponds to a pulse duration of approximately 44 fs. For molecules with smaller rotational constants longer pulses can be used to obtain the same result. The smallest oscillations in alignment with respect to the maximum value corresponds, in Fig. 2, to the weakest pulse train. However, the stronger the pulse train the larger the alignment. This implies that a compromise can be found between maximum alignment and minimum misalignment. On the other hand, for a single pulse with longer duration (right panel of Fig. 2), the alignment oscillates considerably for $\omega_{\parallel} = 250$ and 125, but for the strongest pulse ($\omega_{\parallel} = 375$) the oscillations are greatly reduced. These two plots illustrate the rich behavior that can be expected for cyclic states.

Figure 3 shows the time evolution of the alignment for several cyclic states of systems with the same σ but

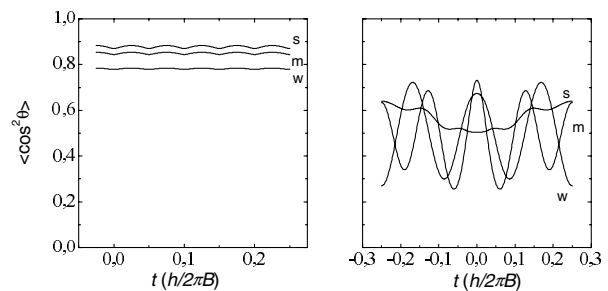


FIG. 2. Alignment, $\langle \cos^2 \theta \rangle$, versus time for a sequence of three identical Gaussian pulses with $\sigma = 0.005$ and $T = 0.05$ (left panel), and a single pulse with $\sigma = 0.05$ and $T = 0.5$ (right panel). Three values of ω_{\parallel} [375(s), 250(m), and 125(w)] were taken for each σ . The cyclic states shown correspond to the following eigenvalues of the (t, t') matrix: -50.98 (s), -31.94 (m), and -13.80 (w) (left); and -4.87 (s), -4.08 (m), and -3.31 (w) (right).

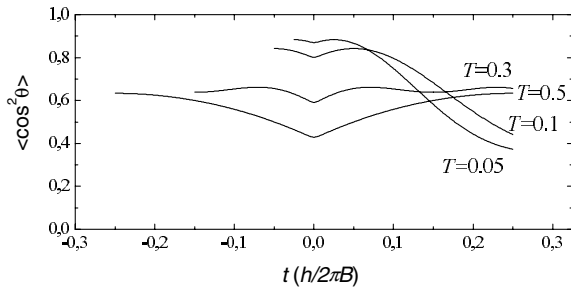


FIG. 3. Alignment, $\langle \cos^2\theta \rangle$, as a function of time, for a single pulse, centered at $t = 0$, with $\sigma = 0.005$ and $\omega_{\parallel} = 375$ for initial wave packets corresponding to cyclic states of (t, t') Hamiltonians for four values of T (10σ , 20σ , 60σ , and 100σ). Notice that for the four curves the evolution from $t = 0.025$ until $t_{\text{final}} = 0.25$ corresponds to effective field-free conditions.

different T values. The evolution between $-T/2$ and $T/2$ is given by Eq. (4) and for $T/2 < t \leq t_{\text{final}}$ has been calculated by field-free propagation. The wave packet for the system with the smallest period ($T = 10\sigma$) gives maximum alignment during the pulse, but the misalignment under field-free conditions (after the time for which the pulse has effectively died, $t \approx 5\sigma$, for realistic fields) is very fast. Since $T = 60\sigma$ corresponds to a case for which the molecule is evolving under field-free conditions for $-30\sigma \leq t \leq -5\sigma$ and for $5\sigma \leq t \leq 30\sigma$, a compromise can be found between maximum alignment during the pulse and long-lasting alignment under field-free conditions. On the other hand, for an initial state corresponding to a cyclic state of $\hat{S}(t)$ with $T = 100\sigma$ the alignment changes more strongly during the pulse. The scheme is really flexible since for the same set of physical parameters B , σ , and ω different values of the period T give rise to generalized Floquet eigenstates with different alignment properties due to the fact that they consist of different combinations of rotational states. It should be realized, when designing an experiment, that the parameter T controls the time delay between pulses.

Two additional conclusions follow from Figs. 1 and 3: (i) if the alignment is substantially conserved for a single pulse during the chosen period, T , a sequence of periodic pulses, $\sum_n \exp[-(t - t_n)^2/\sigma^2]$, where $t_n = nT$, $n = 0, 1, 2, \dots$ will maintain large alignment until $t = (n + 1)T$, and (ii) for a single pulse, aligned initial states corresponding to a (t, t') Hamiltonian with T large compared to σ give rise to field-free alignment during a time approximately equal to $T/2 - 5\sigma$. For the case $T = 60\sigma$, shown in Fig. 3, this corresponds to 15 times the pulse duration.

Summarizing, a new type of states has been found for which a large degree of alignment can be maintained during a single nonresonant laser pulse and a periodic

sequence of identical pulses, suggesting a novel strategy for controlling molecular rotation. Investigation of “non-spreading” cyclic states should be extended to other systems such as asymmetric tops, for which the (t, t') matrix is much larger; molecules in an infrared continuous-wave field [18]; polar molecules interacting with half-cycle pulses in the terahertz range, that give rise to orientation instead of alignment [19]; and elliptically polarized laser fields that can produce three-dimensional alignment [20].

Further work in related fields is needed. For example, nonlinear dynamics studies, such as those discussed in [6] could help to unravel the nature of these new states. Also, the intriguing relation between instantaneous Floquet states and generalized Floquet eigenstates pointed out in [13] could be studied by doing experiments on the systems here analyzed.

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