Multiconfigurational pseudo-Hartree approach for the (t,t') propagator of a molecule in short laser fields

Juan Ortigoso
Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006 Madrid, Spain
(Received 2 July 2004; published 15 November 2004)

A method to study the rotational dynamics of a molecule interacting with a single short laser pulse or a train of pulses is proposed. The method is based on the observation that for such pulses the time propagator, in the (t,t') formalism, can be expressed as a function of approximate Floquet states given by eigenstates of the one-period time-averaged rotational Hamiltonian multiplied by appropriate Fourier functions for the t' coordinate. Each zeroth-order eigenstate can be improved by diagonalizing a small configuration-interaction matrix formed from virtual Hartree-type wave functions. The resulting approximate propagators are more efficient than the usual sudden propagator as they allow one to obtain, in a single step, the propagated wave function at the end of the last pulse of a pulse train.

DOI: 10.1103/PhysRevA.70.055401 PACS number(s): 33.80.−b, 42.50.Hz

Molecular alignment and orientation in laser fields has attracted increasing attention [1] since Friedrich and Herschbach [2] showed theoretically that large alignment can be obtained when a molecule is subject to an intense nonresonant laser pulse. Depending on the intensity and duration of the laser and the rotational constant of the molecule the time evolution can be fully adiabatic or nonadiabatic [3]. In the nonadiabatic case field-free alignment is possible as the molecule ends up after the pulse dies in a rotational wave packet that gives rise to revivals in the alignment. Recently [4] it has been shown that trains of such pulses properly timed can create robust and enhanced alignment. Also, it has been shown [5] that rotational wave packets corresponding to cyclic states of the (t,t') Hamiltonian [6] produce sustained alignment when submitted to a periodic pulse train.

Although efficient methods exist to solve the time-dependent Schrödinger equation [7] for simple systems such as a diatomic molecule in a linearly polarized laser field, their effectiveness is greatly reduced when the complexity of the system increases (see Refs. [8–10] for recent studies on polyatomic systems). The need for fast algorithms is especially acute as normally the Schrödinger equation must be solved iteratively to implement any of the many varieties of quantum control algorithms [11].

Methods for solving the time-dependent Schrödinger equation based on the use of an extended Hilbert space which includes time as a coordinate [6] are being actively studied, as they allow one to overcome the time-ordering problem for the propagator. Thus, it is possible to use the arsenal of numerical methods developed for time-independent systems. For example, perturbative expansions of the (t,t') propagator have been studied recently at great length [12]. Also, a high-frequency treatment of the Floquet problem has been proposed in which the rotational degrees of freedom are adiabatically separated from the fast oscillations of the laser field [13].

In the (t,t') formalism a wave function can be written as an expansion in the basis set of generalized Floquet eigenstates of the operator $S(t')=-i\hbar\,\partial/\partial t'+H(t')$. By taking advantage of the periodicity of the eigenvalues and eigenvectors of $S(t)$ a wave function that obeys $S(t)\psi(t)=0$ can be expanded as a function of the Floquet states ϕ_{ϵ_j} belonging to the first Brillouin zone ($\epsilon_j \in [-\pi/T, \pi/T]$), with T the period chosen for the pulse [14,15]:

$$|\psi(t)\rangle = \sum_{j'} \exp[-i\epsilon_{j'}(t-t_0)/\hbar]|\phi_{\epsilon_{j'}}(t)\rangle\langle\phi_{\epsilon_{j'}}(t_0)|\psi(t_0)\rangle, \tag{1}$$

where the inner product is taken in the Hilbert space corresponding to the zeroth-order spatial Hamiltonian. For strong perturbations the number of time basis functions needed to obtain converged results may lead to a very large Floquet matrix. In this case, it is more advantageous to diagonalize, instead of $S(t)$, the time evolution operator, as explained in detail by Moiseyev in Ref. [16]. Thus, the number of Fourier time functions needed to represent the time evolution operator, even for very strong perturbations, is small for a sufficiently short time interval, which can be always achieved by breaking the whole time interval into a sequence of identical small steps [6,16].

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 to eliminate the fast oscillations of the laser, is [3]

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

where B is the rotational constant, $\mathbf{J}$ is the angular momentum operator, $\alpha_\parallel$ and $\alpha_\perp$ 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 $g(t)$ is chosen to be a Gaussian centered at $t=0$, $\exp(-t^2/\sigma^2)$, characterized by a full width at half maximum of $\tau \cong (5/3)\sigma$ (the pulse duration). The eigenstates of $H(t)/B$ depend on dimensionless interaction parameters $\omega_\parallel = E_0^2\alpha_\parallel/(4B)$ and $\omega_\perp = E_0^2\alpha_\perp/(4B)$. The dimensionless form

of $H(t)/B$ suggests using $\hbar/B$ as a reduced unit of time and $B/\hbar$ as a reduced unit of frequency [3].

Vorobeichik and Moiseyev [17], following Gavrila's work [18] on high-frequency Floquet problems, showed that the eigenstates of the generalized Floquet operator describing the tunneling process in a periodic double-well potential are well approximated by one eigenfunction $\phi_k^0(\theta)$ of the time-independent operator $\int_{-T/2}^{T/2} H(t)dt$, multiplied by one appropriate basis function for the t' coordinate—i.e., $\psi_{km}^0 = \phi_k^0 e^{i2\pi nt'/T}$. The eigenvalues of the zeroth-order Floquet operator are, in this approximation, $E_{kn}^0 = E_k^0 + 2\pi n\hbar/T$ where $k=1,2,...$ and $n=0,\pm1,\pm2,...$.

The present Brief Report is based on the observation that the interaction of molecular polarizability with the *envelope* of a nonresonant pulse can be considered a high-frequency perturbation for a sufficiently short pulse ($\sigma \leqslant 0.005\hbar/B$). This implies that simple Gavrila-type zeroth-order wave functions, such as those of Ref. [17], give good approximations to the eigenstates of the (t,t') matrix corresponding to the Hamiltonian, Eq. (2). These zeroth-order wave functions can be further optimized by doing a Hartree-type separation of the Floquet eigenvalue problem [see Eqs. (3) below]. Diagonalization of the (t,t') Hamiltonian in a small basis set of selected virtual Hartree-type wave functions allows further improving of each approximate Floquet eigenstate at a very low cost.

It should be taken into account, to evaluate the method, that for a single ultrashort pulse the propagator in the sudden approximation [19], $U(t_f,t_0) = \exp[-(i/\hbar)B\mathbf{J}^2 t_f]\exp[i(\omega_\parallel - \omega_\perp)\cos^2\theta]A$, where $A = \int_{-T/2}^{T/2} \exp(-t^2/\sigma^2)dt$, gives excellent results, so the utility of the present approach could be questioned. However, for a periodic pulse train the use of the sudden approximation is not convenient as it gives the evolved wave function only until the end of the first pulse of the sequence. The resulting wave function must then be submitted as initial state for a new propagation corresponding to the second pulse, etc. On the other hand, the approximate (t,t') propagator allows one to calculate the wave function at the end of the last pulse of the train in a single step. Another deficiency of the sudden approximation is that it is appropriate only for times near the end of each pulse of the sequence, while the approximate propagator gives a qualitatively correct wave function at all times.

There are similarities between the present approach and that studied in Ref. [13]. Both methods propose approximate treatments for the Floquet eigenvalue problem of molecules in intense fields. However, Keller, Dion, and Atabek used an adiabatic separation between the fast degree of freedom [the t' dependence of the oscillating term $\cos^2(2\pi\nu t')$] and the slow rotational degree of freedom. This is valid for a continuous field or for a slow-varying pulse envelope. Therefore, the method is useful for adiabatic perturbations due to a long pulse with a central frequency ν that does not need to be extremely high. In the present approach the frequency of the fast oscillating term $\cos^2(2\pi\nu t)$ is considered to be so high that it can be eliminated by simply averaging over the period of the pulse, giving the Hamiltonian, Eq. (2). Then, the method uses a Hartree-type separation between the t' dependence of the laser envelope and the rotational degree of freedom. Therefore, the present scheme is appropriate to study nonadiabatic interactions due to very short lasers.

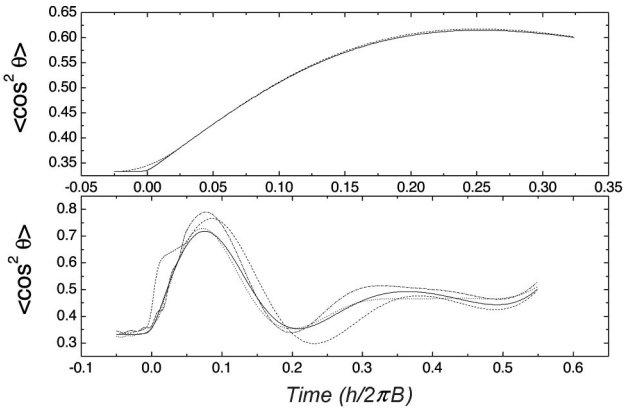

FIG. 1. Time evolution of the alignment, $\langle\psi(t)|\cos^2\theta|\psi(t)\rangle$, with $\psi(t)$ given by Eq. (1), during a single pulse and further field-free evolution for an initial state $|J=0\rangle$. Upper panel corresponds to a pulse with $\sigma=0.005$, $T=0.05$, $\omega_\parallel=200$, and $\omega_\perp=0$. Lower panel is for a pulse with $\sigma=0.01$, $T=0.1$, $\omega_\parallel=400$, and $\omega_\perp=0$. Solid lines correspond to the exact $\psi(t)$ built from eigenvectors obtained by diagonalizing the Floquet matrix in a basis set composed by the product of 8 $|J\rangle$ states and 41 $e^{i2\pi nt'/T}$ states (upper panel) and 11 $|J\rangle$ states and 81 $e^{i2\pi nt'/T}$ states (lower panel). Dashed lines are calculated with approximate $\psi(t)$ functions (see text). In the lower panel the dash-dotted line is calculated with $\psi(t)$ given by eigenfunctions resulting from a multiconfigurational calculation (see text) with $\Delta k=2$, $\Delta n=4$, and $\Delta\epsilon=1000$. The dotted line corresponds to $\Delta k=3$, $\Delta n=6$, and $\Delta\epsilon=1000$.

Figure 1 shows, for the initial state $|J=0\rangle$, the time evolution of the alignment, $\langle\psi(t)|\cos^2\theta|\psi(t)\rangle$. For the exact results, $\psi(t)$ was calculated using Eq. (1) with ϕ_{ϵ_j}'s resulting from diagonalizing the Floquet matrix in the $|J\rangle e^{i2\pi nt'}$ primitive basis set. The approximate results correspond to a $\psi(t)$ wave function calculated by using Eq. (1) where each ϕ_{ϵ_j} was replaced by one eigenfunction of $\int_{-T/2}^{T/2} H(t)dt$ multiplied by one $e^{i2\pi nt'}$ function. The upper panel corresponds to a pulse with $\sigma=0.005$ and it shows almost perfect agreement between the approximate and the exact evolution except for the earlier times of the pulse. The agreement is also very good after the pulse dies for the further field-free evolution. The lower panel corresponds to a longer and more intense pulse. In this case the agreement is worse but still the time evolution of the alignment is qualitatively well calculated by using an approximate $\psi(t)$. The simplicity of the approximate calculations should be realized. They require only the diagonalization of the rotational matrices corresponding to the one-period-averaged Hamiltonian—i.e., a 8×8 matrix (upper panel) or 11×11 matrix (lower panel). Zeroth-order $\psi(t)$ functions depend on the quality of the approximate eigenfunctions and eigenvalues of $S(t)$. Thus, for the calculation corresponding to the shorter pulse in Fig. 1 the exact Floquet states that give a greater contribution to the dynamics are (in $B/\hbar$ units) $\epsilon_1=-24.5$, $\epsilon_2=-6.3$, and $\epsilon_3=5.1$. The approximate Floquet eigenvalues are $\epsilon_1=-24.6$, $\epsilon_2=-6.4$, and $\epsilon_3=5.0$. For the longer pulse shown in Fig. 1 the agreement is not that good. (Exact ϵ's are -24.6, -21.3, -3.5, and 8.8.

Approximate ϵ's are −26.0, 11.0, −4.9, and 7.7.) These approximate zeroth-order eigenstates are given in this approach by only one basis function, while their composition in the primitive basis $|J\rangle e^{i2\pi nt/T}$ is more complex. For example, the eigenstate $\epsilon_1=8.8$ $[\phi^0_{J=0}(\theta)|n=1\rangle]$ is given by a linear combination of 15 primitive basis functions $|J,n\rangle$ (with J values between 0 and 6 and n between −1 and 5).

Zeroth-order (t,t') wave functions can be improved by using second-order perturbation corrections. This kind of perturbative treatment is "expected to give good results when the frequency of the field is larger than a classical frequency of the system in the time-averaged potential" [17]. Instead of the perturbative treatment, it is shown in the next paragraphs that each approximate Floquet eigenstate can be improved by diagonalizing a matrix representation of $S(t)$ built up from a few selected zeroth-order basis functions. Further reduction of the (t,t') matrix can be achieved by using improved zeroth-order basis functions resulting of a Hartree-type separation of the eigenvalue Floquet problem. This can be achieved by realizing that the original eigenvalue problem can be formally divided into two eigenvalue problems as in the self-consistent method:

$$[B\mathbf{J}^2 - \Delta\omega\langle\chi(t')|\exp(-t'^2/\sigma^2)|\chi(t')\rangle\cos^2\theta]\phi(\theta) = \epsilon_\theta\phi(\theta),$$

$$\left[-i\frac{\partial}{\partial t'} - \Delta\omega\langle\phi(\theta)|\cos^2\theta|\phi(\theta)\rangle\exp(-t'^2/\sigma^2)\right]\chi(t') = \epsilon_{t'}\chi(t'), \tag{3}$$

where $\Delta\omega=\omega_\parallel-\omega_\perp$. Both eigenvalue problems can be solved by diagonalizing small matrices. The total energy in this approximation is

$$\epsilon = \epsilon_\theta + \epsilon_{t'} - \langle\phi(\theta)\chi(t')| - \Delta\omega\cos^2\theta e^{-t^2/\sigma^2}|\phi(\theta)\chi(t')\rangle,$$

and the total wave function is simply $\phi(\theta)\chi(t')$. The term pseudo-Hartree was used in the title because this approach is not really self-consistent for the particular problem studied here, since the matrix element $\langle\chi(t')|\exp(-t^2/\sigma^2)|\chi(t')\rangle$ is a constant independent of $\chi(t')$. Consequently the method is not able to use the information on the t' wave function to improve the rotational eigenfunction. However, a (t,t') matrix built from these basis functions leads to better eigenfunctions than a matrix built from Gavrila-type zeroth-order basis functions, as the $\chi(t')$ basis functions are linear combinations of the $e^{i2\pi nt'/T}$ functions. Notice that the rotational Hartree-type wave functions are the same as the corresponding to the one-period-averaged Hamiltonian, but the t' functions depend on the shape of $\phi(\theta)$. Therefore, the procedure is the following: (i) Chose, as initial states for Eqs. (3), $\phi(\theta)=|J\rangle$, $\chi(t')=e^{i2\pi nt'/T}$ for the different $|J\rangle$ states in the primitive basis set, with n such that the quasienergy for $\phi(\theta)\chi(t')$ belongs to the first Brillouin zone, (ii) obtain a set of virtual $\phi(\theta)$ and $\chi(t')$ functions after the first iteration of the method for each J value, (iii) for each initial $|J\rangle$ state construct a configuration-interaction (CI) (t,t') matrix by selecting a subset of the $\phi_k(\theta)\chi_n(t')$ and diagonalize to obtain an improved Floquet state, (iv) orthogonalize the eigenstates corresponding to the different J values, and (v) build the propagator. The selection of the basis functions in step (iii) could be optimized by using artificial intelligence methods [20], but a simpler way was chosen consisting of fixing two thresholds (Δk and Δn) in the quantum numbers, and another one in the energy ($\Delta\epsilon$) as was suggested for rovibrational problems in Ref. [21].

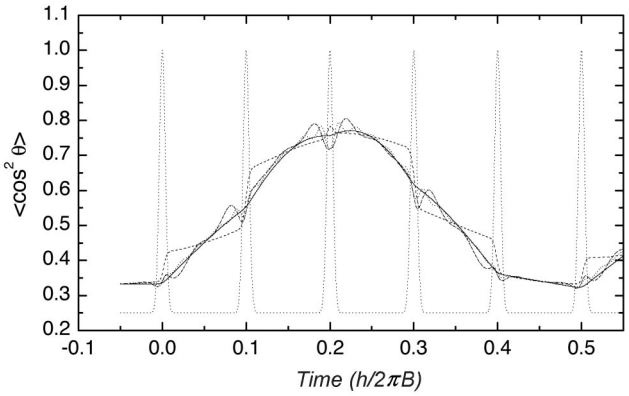

FIG. 2. Time evolution of the alignment for the initial state $|J=0\rangle$ in a pulse train consisting of six pulses. Parameters defining each pulse are $\sigma=0.005$, $\omega_\parallel=250$, and $\omega_\perp=0$. The period chosen in the calculation was $T=0.1$. The different curves are exact evolution (solid line), zeroth-order propagation (dashed line), CI-Hartree propagation with $\Delta k=1$, $\Delta n=2$, and $\Delta\epsilon=1000$ (dash-dotted line), and CI-Hartree calculation with $\Delta k=2$, $\Delta n=4$, and $\Delta\epsilon=1000$ (dotted line).

Figure 1 (lower panel) shows the convergence of the calculation to the exact alignment for a single pulse when the basis set of zeroth-order wave function increases. For the smallest basis sets (dash-dotted line) the calculation shows, at the beginning of the pulse, oscillations in the alignment that indicate that the approximate Floquet eigenstates are linear combinations of the exact eigenstates. When the basis set is slightly increased (dotted curve) the CI calculation converges toward the exact alignment. For this calculation the maximum size of the matrices diagonalized for one approximate eigenstate was 91, while the size of the (t,t') matrix in the primitive basis set was 891. The eigenvalues of the Floquet states that contribute to the time evolution for the CI calculation with thresholds $\Delta n=3$, $\Delta k=6$, and $\Delta\epsilon=1000$ are −23.8, −20.9, −3.5, and 9.0 (compare these numbers with those given above). The eigenvalue corresponding to the exact eingenstate $\epsilon=8.8$ is now $\epsilon=9.0$, and it is given, in the CI basis set, by $\phi^{CI}(\theta,t')\approx-0.95\phi_{J=0}\chi_{50}(t')+0.19\phi_{J=2}\chi_{49}(t')+0.12\phi_{J=4}\chi_{49}(t')-0.17\phi_{J=6}\chi_{49}(t')$, where $\phi_J,\chi_l(t')$ are the eigenfunctions of Eqs. (3), and l indicates the energy ordering.

Figure 2 illustrates the results of this procedure for a pulse train consisting of six short pulses well separated in time. The zeroth-order propagation (dashed line) is able to reproduce qualitatively the general trend of the time evolution during the whole range of the problem. The propagations done with CI-Hartree-type functions improve the curves, and the dotted line is almost indistinguible, at the plot resolution, in many regions, from the exact calculation. The maximum number of Hartree-type basis functions needed to build the largest CI matrix for this case was only 45.

In the (t,t') method the number of primitive basis functions needed to get a correct propagator increases with the ratio T/σ. For a single pulse it is enough to choose a T value for which the electric field is effectively zero. However, the parameter T has a physical meaning for a pulse train, representing the delay between pulses, and it can be chosen as large as desired [5]. Figure 3 shows results for a sequence of three pulses with a large time delay between them corresponding to a large T/σ value and, therefore, it represents a difficult test for the method. Notice that the approximated time evolution of the alignment during the first pulse is much worse than that shown in Fig. 1 (for the same σ) due to the larger period chosen now. However, more primitive functions were also needed to obtain the exact results ($11|J\rangle$ states and 101 time Fourier functions).

Summarizing, a simple method is proposed to calculate the time evolution of molecular alignment in periodic trains of short laser pulses. The method gives, for a single pulse in the impulsive regimen, results of quality similar to the sudden approximation. However, the method is more convenient, for pulse trains, than the sudden approximation, since the propagation can be done in a single step for the whole time interval.

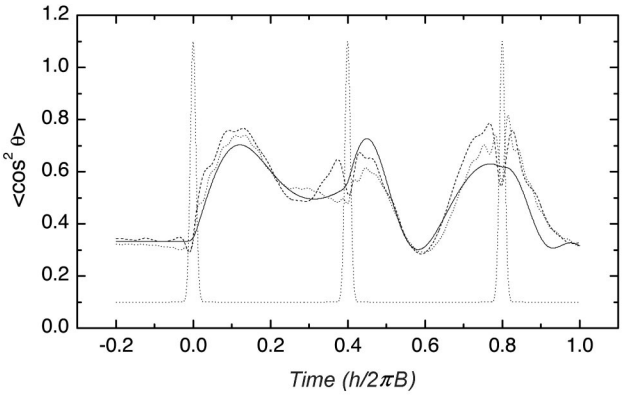

FIG. 3. Time evolution of the alignment for the initial state $|J=0\rangle$ in a sequence of three pulses with $\sigma=0.01$, $\omega_{\parallel}=250$, and $\omega_{\perp}=0$. The period chosen in the calculation was $T=0.4$. The different curves are exact evolution (solid line), CI-Hartree propagation with $\Delta k=2$, $\Delta n=6$, and $\Delta\epsilon=200$ (dashed line), and CI-Hartree calculation with $\Delta k=3$, $\Delta n=12$, and $\Delta\epsilon=200$ (dotted line).

Financial support from the Ministerio de Ciencia y Tecnología of Spain, under Project No. BFM2001-2315 is acknowledged.

[1] H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2003).
[2] B. Friedrich and D. Herschbach, Phys. Rev. Lett. **74**, 4623 (1995).
[3] J. Ortigoso, M. Rodríguez, M. Gupta, and B. Friedrich, J. Chem. Phys. **110**, 3870 (1999).
[4] M. Leibscher, I. Sh. Averbukh, and H. Rabitz, Phys. Rev. Lett. **90**, 213001 (2003); Phys. Rev. A **69**, 013402 (2004).
[5] J. Ortigoso, Phys. Rev. Lett. **93**, 073001 (2004).
[6] U. Peskin and N. Moiseyev, J. Chem. Phys. **99**, 4590 (1993).
[7] M. D. Feit, and J. A. Fleck, Jr., J. Chem. Phys. **78**, 301 (1983).
[8] J. J. Larsen *et al.*, Phys. Rev. Lett. **85**, 2470 (1999).
[9] E. Péronne *et al.*, Phys. Rev. Lett. **91**, 043003 (2003).
[10] M. D. Poulsen *et al.*, J. Chem. Phys. **121**, 783 (2004).
[11] S. A. Rice, and M. Zhao, *Optical Control of Molecular Dynamics* (Wiley, New York, 2000).
[12] D. Sugny *et al.*, Phys. Rev. A **69**, 043407 (2004).
[13] A. Keller, C. M. Dion, and O. Atabek, Phys. Rev. A **61**, 023409 (2000).
[14] A. N. Seleznyova, J. Phys. A **26**, 981 (1993).
[15] G. Jolicard and J. P. Killingbeck, J. Phys. A **36**, R411 (2003).
[16] N. Moiseyev, Comments At. Mol. Phys. **31**, 87 (1995).
[17] I. Vorobeichik and N. Moiseyev, Phys. Rev. A **59**, 2511 (1999).
[18] *Atoms in Intense Laser Fields*, edited by M. Gavrila (Academic, New York, 1992).
[19] N. Henriksen, Chem. Phys. Lett. **312**, 196 (1999); C. M. Dion, A. Keller, and O. Atabek, Eur. Phys. J. D **14**, 249 (2001).
[20] J. Ortigoso, G. T. Fraser, and B. H. Pate, Phys. Rev. Lett. **82**, 2856 (1999).
[21] J. Makarewicz, A. Wierzbicki, and J. Koput, Chem. Phys. **97**, 311 (1985).